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STABLE OXYGEN AND SULFUR ISOTOPES APPLIED TO TRACING SEEPAGE FROM MINE TAILINGS

by

Kimberly Sue Ries

A Thesis Submitted to the Faculty of the

DEPARTMENT OF HYDROLOGY AND WATER RESOURCES

In Partial Fulfillment of the Requirements
For the Degree of

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In the Graduate College

THE UNIVERSITY OF ARIZONA

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APPROVAL BY THESIS DIRECTOR

This thesis has been approved on the date shown below:

Austin Long

AUSTIN LONG
Associate Professor of Geosciences

7 Dec 82
Date

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ABSTRACT

Sulfur and oxygen isotopes in dissolved sulfates were used to trace seepage from a uranium tailings pond into a shallow alluvial aquifer. Twenty-two wells, 2 tailings ponds, and an adjacent stream were sampled on and nearby the Kerr-McGee Nuclear Corporation section 31 millsite at Ambrosia Lake, New Mexico. The isotopic analyses showed significant isotopic differences between acid pond sulfates contributed by the mill process and natural sulfates in the local ground waters. Three distinct groups of waters were identified in the alluvial system at different points downgradient from the millsite, pond leachate, mine discharge, and Tres Hermanos formation waters. This distinct grouping of waters would not have been possible based only on chemical data. Isotope results also provided clues to the types and extent of geochemical interactions occurring as water travels from ponds into an aquifer system.

CHAPTER 1

INTRODUCTION

Conclusive evidence of seepage from unlined tailings impoundments into shallow aquifers may be difficult to obtain from standard chemical and hydrologic data. Monitoring well systems near tailings impoundments are required to obtain mill operating permits, but these wells may fail to intercept seepage plumes. If accurate monitor well patterns are established so that seepage plumes may be sampled, the chemical and physical characteristics of the original tailings effluent may be so drastically altered that seepage is not easily identified. Contamination may also be difficult to detect if ground waters sampled in these highly mineralized mining areas contain naturally high concentrations of major and trace ions and show large natural chemical variations within a small area.

Even if an effective pattern of monitoring wells has been established, it becomes important for monitoring purposes to find a "tracer" unique to the tailings ponds that remains unaltered as it travels with the seepage plume. This study tested the use of sulfate isotopes as a ground-water tracer at the Kerr-McGee Nuclear Corporation section 31 millsite in the Ambrosia Lake uranium mining district near Grants, New Mexico.

The sulfate ion is a major constituent in possible sources of ground-water contamination from mine wastes, mill tailings ponds, and many industrial discharges. This anion travels generally unimpeded along ground-water flow paths, and sampling and analyses are straightforward. Despite these attributes, the major obstacle in using sulfate as a tracer in the area studied is its relatively high concentration in natural uncontaminated ground-water systems. This problem is eliminated if there is some means to distinguish between different sulfate sources.

In this study stable sulfate isotopes were used as a way to distinguish sulfate sources, thus providing an inexpensive reliable tracer for a variety of contaminant monitoring situations. The present study involved characterization of seepage from unlined uranium mill tailings impoundments within the richly uraniferous Ambrosia Lake mining district. The 7,000 ton-per-day Kerr-McGee uranium mill is the largest in the United States, and like most uranium mills, it leaches uranium from crushed ore using a sulfuric acid solution. Waste slurry from the mill, composed of a solid portion of sands and clayey chemical precipitate slimes, and a liquid portion rich in dissolved ion and trace metals, is pumped to a series of lined and unlined ponds for decantation and evaporation. The waste liquid, containing nearly 37,000 mg/L sulfate mixed with other processing chemicals and elements solubilized from the ore, either evaporates, is retained in the solid tailings as interstitial water or seeps into the subsurface.

In this study, it was hoped that the chemical sulfate H_2SO_4 used in the acid leach mill circuit would carry a characteristic isotope label on both sulfur and oxygen relative to the natural or background sulfates dissolved in the local ground waters. If so, the sulfate collected from monitoring wells could be isotopically analyzed to show the relative importance of pond contaminant sources at different locations around the millsite and mixing equations could be used to calculate percentage of pond leachate in monitoring well samples.

Like most water-quality monitoring situations, the water-quality aspects of mining, milling, or industrial operations are not limited to a single localized contaminant source such as a waste impoundment. Uranium industry effluents, which may travel into shallow ground-water systems, include not only mill process effluents (tailings) but also mine dewatering effluents and non-point source effluents like precipitation runoff from ore and waste-rock piles. The Ambrosia Lake district has had the longest sustained discharge of effluents (since the early 1950s) in the Grants Mineral Belt, making it one of the most complicated mining areas in which to determine certain water-quality impacts from the uranium industries (Gallaher and Goad, 1981). Publically accessible data of discharges and water-quality criteria were not systematically gathered until the mid 1970s. Such a limited data base has made it impossible to evaluate the relative importance of all possible contaminant sources (Gallaher and Goad, 1981).

To better understand these possible contaminant sources and more effectively utilize existing costly monitor well programs, the Kerr-McGee Nuclear Corporation participated with the New Mexico State Environmental Improvement Division (EID) and me in collecting samples and providing pertinent information for this study. Funding was provided by the Pueblo of Laguna, New Mexico. Analyses of sulfur and oxygen isotopic composition of dissolved sulfates from a mill tailings pond, a tailings solution evaporation pond, a mine effluent storage reservoir, a stream, and 22 monitoring wells were used to detect seepage of mill effluent and mine dewatering discharge into an alluvial system. Additional isotope analyses were made of the oxygen-18 in collected water samples, and major ion and trace-metal analyses were performed by EID. Permission to incorporate these data into this thesis was granted by Bruce Gallaher of the Groundwater Pollution Control Division of the New Mexico State EID.

Purpose of Study

The purpose of the study was to test the effectiveness of sulfate isotopes in tracing seepage from unlined tailings impoundments. If isotopic labeling of dissolved sulfates can distinguish their source, then sulfate isotopes could provide an ideal conservative tracer for a variety of contaminant monitoring situations.

Sulfate isotopes may not only act as indicators of source waters but may also provide clues to the geochemical history of the dissolved sulfate. Variations in sulfate isotopes provide clues to sulfate sources and the geochemical processes producing dissolved sulfate.

The differences in ^{34}S and ^{18}O ratios of dissolved sulfates in water samples taken within a 2-mile area around a millsite were used to detect seepage migration from unlined tailing ponds into a shallow alluvial ground-water system.

Rationale for Study

This is the first study to apply the isotopic composition of sulfates to tracing seepage from a tailings impoundment. For this reason a discussion of sulfate isotopes as tracers with regard to this unique application is included. First, a brief review of general ground-water tracing theory is presented, followed by a look at the use of sulfates and their isotopes as tracers. A review of the previous investigations using sulfate isotopes shows this study is a natural extension of isotope tracing work for a situation where most other tracers have proved unsuitable and where high sulfate concentrations exist in the water of interest.

Ground-water Tracing Theory

A hydrologic tracer is a constituent or property of a fluid that helps characterize its movement through a porous or fractured medium (Davis and others, 1980). Under this definition, a tracer can either give information about the medium of transport or about properties of the fluid in motion such as direction or velocity. Tracer selection is based on the type of information required, the hydrologic system of interest, and the ease and economics of its application. Pond seepage tracing requires a tracer that gives information about the velocity, direction, and potential contaminants that could be transported in seepage plumes. This type of tracer is referred to as "conservative," in that it travels with the fluid through a conductive medium without being significantly retarded. An ideal conservative tracer must remain chemically stable and unreactive as it travels in a system without altering the natural fluid flow direction or velocity. Hydrologic tracers can be purposely introduced into a system or they can be a natural part of the system.

The value of tracers in understanding and modeling hydrologic flow systems has prompted researchers to identify suitable tracers. It was natural to look for constituents such as major dissolved ions and trace constituents that traveled in normal ground-water flow systems. Cations are susceptible to sorption on solid materials in the aquifer; metals and other trace constituents are commonly unstable and susceptible to chelating or precipitation and are more difficult to detect. Anions such as Cl^-, NO_3^-, and SO_4^{2-} are the group of ions most suitable to conservative tracing due to low sorption and ease of detection. However, high natural background concentrations limit their use in many tracing applications. The use of tagged radioactive tracers is normally prohibited by state and federal regulations. Gases dissolved in water present their own problems with handling, analyses, and natural background concentrations. Long lists have been compiled of man-made compounds such as fluorinated organic anions and neutral fluorcarbons that have been used or designed for specific hydrologic applications (Thompson and Stetzenbach, 1980). Major drawbacks in their widespread use are high cost and sophisticated analytical methods. Although each of these tracer groups has been mentioned with regard to its problems in widespread applications, each finds satisfactory application in certain hydrologic situations.

Another generalized group of tracers is the stable isotopes, the tracer type applied in this field study. The natural variations in the isotopic composition of some elements, ^{1}H-^{2}H, ^{12}C-^{13}C, ^{14}N-^{15}N, and ^{16}O-^{18}O, can be used to identify sources of dissolved constituents in ground-water samples. The need for specialized analytical equipment and high costs for analyses have limited the widespread use of these isotopes, but the ever-expanding areas of study and the applications of stable isotopes are increasing the number of laboratories, the bulwark of data, and the framework of knowledge about stable isotopes.

Use of Stable Isotopes as Tracers

Isotopic labeling involves the introduction of a material that is isotopically different, but chemically identical to that normally found in the system (Curtis and Gancarz, 1978). In this context, isotopes of elements in commonly dissolved ground-water constituents can identify different sources for these chemical species, their mixing patterns, and the general ground-water flow directions. The commonly dissolved chemical species such as the anions Cl^-, SO_4^{2-}, and NO_3^- that travel intimately with ground water can be used as tracers if sufficient isotope variation exists between the tracer and the background constituents.

An isotope tracer such as sulfur-34 is independent of the absolute concentration of its carrier species, SO_4^{2-}. Barring any fractionating mechanisms, the isotopic signature remains unchanged despite any physical or chemical processes that may change the concentration of its carrier. Changes in isotope ratios can then only result from mixing with another carrier of a different isotope ratio. It is only the relative abundance of the isotopically labeled carriers and the efficiency of mixing that determines the measured isotope ratio. As more data on stable isotope ratios are obtained, a better understanding of sources and geochemical histories of dissolved ground-water species can be established.

Hydrologic Tracing Scenario. The Kerr-McGee uranium mill, along with all but one other mill in the Grants Mineral Belt, employs a sulfuric acid leaching circuit to extract uranium from the mined crushed ore (Kunkler, 1979). This results in inordinately high sulfate concentrations in uranium mill tailings disposal ponds (37,000 mg/L in the Kerr-McGee pond #1 on November 9, 1981). The unlined ponds upon which this study focused are constructed upon alluvium generally less than 7 ft (2 m) thick composed mostly of silt, sand, and clay and underlain by sandstones and shale units of the Mancos Formation (New Mexico State Engineer's Office, 1979). The maximum area of unlined ponds (Nos. 1-10) reported in 1975 was 234 acres; the estimated seepage over this area was 203 gpm (Ganus, 1980). The actual area of the ponds and their depth and usage have been constantly changing over their 13-year history, but roughly a third of the liquid discharged to the ponds is lost through seepage.

The alluvial system's sources of recharge to the alluvium are not confined to just pond seepage and sparse precipitation events. Thus the hydrologic tracing situation is not so clearly defined due to (1) long-term (since 1951) seepage of uranium industry effluents, (2) many sources of uranium effluents from different mines and mills in the localized area, and (3) the difficulties of predicting geochemical interactions that occur along ground-water flow paths. The situation requires a tracer that has been in the system for a long time, can be distinguished from any background or natural constituents, and has a relatively simple geochemical history.

Mechanisms of Sulfate Removal. To use sulfate isotopes as tracers, the geochemical interactions that may remove sulfate as it travels from the ponds into a ground-water system must be understood. Extreme variations in chemical conditions such as pH, Eh, and ionic strength exist between the tailings solution ponds and the alluvial ground waters. As seepage from ponds percolates into the subsurface, its dissolved constituents undergo many hydrogeochemical reactions to establish new chemical equilibria with the existing conditions. In the process many species formerly in solution under acidic (pH 1 to 2) pond conditions are precipitated, sorbed onto solid phases, or exchanged with other mineral species. Because the isotope ratio on sulfate may be a function of relative mixing proportions of two or more distinct sulfate sources, the types of mechanisms that may remove sulfate from solution are important to understand.

As pond seepage leaches through the foundation material, the subsoil acts to neutralize the acid as expressed by the reaction:

$$2H^+ + SO_4^{2-} + CaCO_3 \rightarrow CaSO_4\downarrow + H_2O + CO_2 \qquad (1)$$

Sulfate is removed by precipitation as gypsum or anhydrite. Kerr-McGee maintains that $CaCO_3$ composes 2 percent of the alluvial material through which seepage travels. By calculations (using SO_4^{2-} = 37,000 mg/L in pond #1) this is sufficient $CaCO_3$ such that all the sulfate could theoretically be removed by precipitation (Rahn and Mabes, 1978).

However, reaction (1) occurs in a complex chemical system in which many other chemical reactions compete for available hydrogen ions, thus allowing much of the sulfate to remain in solution. Anhydrite commonly precipitates, forming a coating on the carbonate matrix materials to prevent further neutralization of the acidic seepage (Morin and others, 1982). After a steady pH and ion population are reached, it is the degree of saturation with respect to sulfate that determines its concentration in solution.

Anions are normally unaffected by sorption mechanisms. However, under a low pH, normally negatively charged clay particle edges may protonate, allowing sorption of negative ions such as sulfate. This would most likely occur in the "slimes" or clayey layer that settles at the bottom of the tailings pond (pond #1). Decant (pond #3) and evaporation (ponds #4–#10) do not contain this solid tailings fraction of mill wastes and are therefore less likely to intercept sulfate by sorption.

Despite these chemical interactions that remove some sulfate from tailings solution, sulfate concentrations in adjacent pond monitor wells range from 3,000 to almost 8,000 mg/L (November 10, 1981) attesting to the mobility of the sulfate anion in seepage from the ponds.

Isotope Labeling. Isotopic composition can vary considerably between different sulfate sources in a ground-water system. If this is the case, each sulfate carries an isotopic label that can identify its source in a particular sample. In this manner, the mill pond acid sulfates can be distinguished from any natural sulfate dissolved in ground waters. The sulfate anion is potentially doubly useful as a tracer because both sulfur and oxygen can be isotopically analyzed to determine their source and to obtain information on the geochemical history of the sulfate. Moreover, sulfate is an isotopically stable anion and will not exchange its sulfur or oxygen atoms at normal ground-water temperatures and pH over a geologically practical span of time.

The premise in utilizing stable isotopes in this application is that significant differences exist between isotope ratios of different sulfate sources. In designing such an isotope tracing study, an initial sampling of suspected sources is recommended to see if the isotope ratios are unique to the system before initiating a full-scale sampling program.

CHAPTER 2

PREVIOUS INVESTIGATIONS

Supporting Literature

A number of investigations have utilized sulfur isotopes to determine the sources of sulfates in natural water systems. Only 12 years after Urey's (1947) classic paper in which he estimated stable isotope fractionation factors, Ostlund (1959) looked at the ^{34}S–^{32}S ratios in rainwater and surface waters to approach the question of the origin of airborne sulfur. Also, in the that year Ault and Kulp (1959) published a paper presenting accumulated sulfur isotope ratios of 500 samples from various geologic settings, including oceans, evaporite deposits, hydrothermal deposits, igneous rocks, meteorites, volcanoes, and biogenic materials. Using these data, they tried to obtain an isotopic material balance of sulfur in the sulfur cycle. More ratios of the isotope composition of natural and anthropogenic sulfur compounds accumulated in the following years. Various reports and their source for sulfate compound ratios include:

1.	Jensen and Nakei (1961)	atmospheric sulfur near industrial areas
2.	Rafter and Wilson (1963)	geothermal and volcanic settings
3.	Holser and Kaplan (1966)	sedimentary sulfates
4.	Longinelli and Craig (1967)	sea water and saline lakes
5.	Cortecci (1973)	oxygen-18 (SO_4^{2-}) variations in Italian lakes

Data indicated that isotope ratio ranges of major sulfur reservoirs overlap so much that net contribution rates from principal sources could not be determined on a global scale (fig. 1) Despite the large isotope ratio overlap in major sulfur reservoirs, sulfur (and oxygen) isotope ratios may be used locally in situations with two to three major sulfur sources with large well-known ratio differences between them so that net contributions can be identified. Hitchon and Krouse (1972) used sulfur isotope values in conjunction with other stable isotopes and chemical data to study the hydrogeochemistry of a single river drainage basin in Canada. In this well-known study, the ratio of stable isotopes of ^{34}S and ^{32}S in dissolved sulfate was measured on 52 surface-water samples to elucidate some of the different origins of sulfate dissolved in the waters. The isotope ratios and chemical results demonstrated the extreme complexity in hydrogeochemical behavior in a single river basin hydrologic unit.

Schwarcz and Cortecci (1974) tried to relate the sulfur as well as oxygen isotopes of sulfates in spring and stream waters to local source environments. They selected remote sampling areas in the Italian Alps and Appennines where little anthropogenic sulfate was likely to be present. In their results, sulfates of similar geologic provenance generally did not show similar isotope ratios.

Studies of ground-water sulfate isotopes are expected to show more uniform values due to mixing and to longer residence times. Rightmire and others (1974) obtained information about the origin of dissolved sulfur species and the flow paths of ground waters in two major U.S. aquifers. Sulfur isotope ratios allowed refinements of

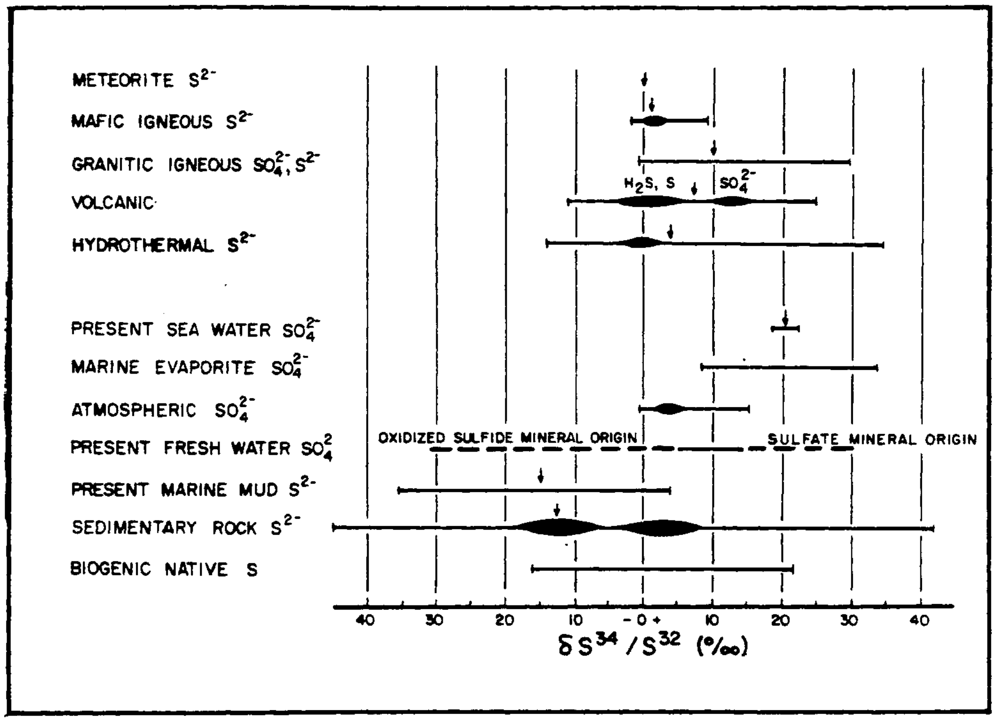


Figure 1. Range in $\delta^{34}S$ for major sulfur reservoirs. -- From Holser and Kaplan (1966, p. 94).

previous geochemical interpretations based only on hydrologic and geochemical information. In another partially understood geochemical situation, oxygen-18 (SO_4^{2-}) measurements were used by Smejkal (1978) in answering the question of sulfate origin in mineral springs. The study of stable sulfate isotopes revealed new criteria for solving the problem. Krothe and Libra (1981) used sulfur isotope data and geochemical data to determine the sources of sulfate in a carbonate terrain and to classify spring-water flow systems as shallow or deep.

This review has presented only a sampling of investigations using sulfate isotopes to determine geochemical origins of sulfur species in natural waters. In comparison, few studies have used sulfur isotopes to trace anthropogenic or point-source sulfur contaminants. Earliest applications involved the use of isotope tracers to understand contributions to and reactions of atmospheric sulfur compounds in the formation of "acid rain." Gray and Jensen (1972) were able to determine the net contribution of major suppliers of sulfur to the atmosphere in the Great Salt Lake area. In this study they had narrow, well-defined sources, including a copper smelter that was both active then inactive during the course of the investigation. In another study, Nriagu and Harvey (1978) used sulfur isotope variations to identify sulfur sources and to trace pathways of sulfur migration in the environment. They studied sulfur pollution of natural waters in lakes at various distances from smelter stacks near Sudbury, Ontario. Similar to this study application, they wished to ascertain point source contributions to variations in isotopic composition of sulfur at different sampling locations.

Background

The discovery of radioactivity and the properties of radioactive substances near the turn of the twentieth century promulgated the discovery of elemental isotopes. Development of mass spectrography by Francis Aston in 1922 to measure the relative mass of atoms of an element led to the discovery of stable isotopes. These identical elements differed only in their atomic weights and were thus expected to differ in physical and chemical properties related to their mass.

In this period of burgeoning nuclear theory, Harold Urey pioneered the development of isotope theory to explain the partitioning of isotopes between elements. Using quantum mechanics and statistical thermodynamics, Urey formulated the theoretical model that explains isotopic distributions between coexisting compounds resulting from differences in their thermodynamic properties. In 1947 Urey published his classic paper of numerical calculations of the equilibrium distribution constants for an incredible number of isotope exchange reactions. From this point, experimental work proceeded to test the calculations based on Urey's model for isotopic fractionation.

Isotopes are defined as atoms of a given element having the same number of protons but different numbers of neutrons and accordingly different atomic masses. They are denoted in the form $^{m}_{n}E$, where m represents the mass number (neutrons + protons) and n the atomic number (number of protons). Isotopes are characteristically divided into stable and unstable (radioactive) species, although "stable" is a relative term depending on the detection limit of radioactive decay times. Nuclear stability depends on the nuclear mass (number of protons and neutrons) and the proton-to-neutron ratio.

Most elements are not "pure" but are made of a mixture of at least two isotopes, which may be present in varying proportions. One isotope generally predominates, the other(s) being present in only trace amounts. Table 1 presents the relative abundance of the stable isotopes of sulfur and oxygen. These global isotope abundances are directly related to the stability of the nuclear configurations and to their production and removal processes over time.

Table 1. Relative abundance of sulfur and oxygen isotopes. -- Data from Hoefs (1980).

Abundance, %			
Sulfur		Oxygen	
^{32}S	95.0	^{16}O	99.759
^{33}S	3.76	^{17}O	0.037
^{34}S	4.22	^{18}O	0.204
^{36}S	0.014		

Isotope Fractionation Mechanisms

In addition to the natural partitioning of isotopes, isotope fractionation processes further separate and redistribute the isotopes of elements. Isotope fractionation is defined as the partitioning of isotopes between two substances of different isotopic ratios (Hoefs, 1980). The ratios of the stable isotopes of an element in reacting compounds are normally different in each compound. Fractionation of isotopes between compounds occurs, according to Urey's isotope theory, because a chemical bond involving a heavy isotope has a lower vibrational frequency than the equivalent bond of the light isotope. The heavy isotope bond has a lower zero-point energy and consequently is stronger than the light isotope bond. For example, Harrison and Thode (1957) studied chemical reduction of sulfate (SO_42-) to hydrogen sulfide (H_2S) and found that $^{32}SO_4^{2-}$ reduced 2.2 percent faster than $^{34}SO_4^{2-}$. Urey and Greiff (1935) first showed that these small differences in chemical properties of isotopes are enough to cause isotope fractionation in the laboratory and in nature. Although Urey (1947) had calculated equilibrium constants for isotope exchange reactions to predict natural fractionation, quantitative agreement between theory and observation cannot be expected. Natural processes are commonly complex and occur in a unidirectional manner, in cyclic paths, or in enzymatically rate controlling steps. If so, equilibrium process fractionations cannot be applied, and reaction kinetics are the principal means for isotope fractionation (Rankama, 1954).

The three main isotope fractionation processes are:

1. Equilibrium processes.
    - a. Physical (evaporation, diffusion).
    - b. Chemical.

2. Kinetic processes.
   a. Physical (diffusion, ultrafiltration).
   b. Chemical.
3. Biologic processes (preference of enzymes for one isotope over another.

Notation for Reporting Isotope Fractionation

The fractionation factor, alpha (α), is defined as the ratio of the numbers of any two isotopes in one chemical compound, A, divided by the corresponding ratio for another chemical compound, B,

$$\alpha_{A-B} = \frac{R_A}{R_B} \qquad \text{for example, } \alpha_{HS^- - H_2S} = \frac{(^{34}S/^{32}S)_{HS^-}}{(^{34}S/^{32}S)_{H_2S}}$$

Alpha is usually defined for equilibrium fractionation processes where an isotope is exchanged in an equilibrium system such as:

$$H_2{}^{34}S + H^{32}S^- \rightleftarrows H_2{}^{32}S + H^{34}S^-$$

Because the ^{34}S bonds are stronger than ^{32}S bonds, the chemical properties of the two species (i.e., $H_2{}^{34}S$ and $H_2{}^{32}S$) are different; therefore the equilibrium constant (K) and α do not generally equal unity. These isotopic equilibrium constants are very slight compared to chemical equilibrium constants, and α is close to unity, typically 1.00x. Fractionations are expressed in terms of the value of x in per mil ($^{\circ}/_{\circ\circ}$) units (Hoefs, 1980). Like chemical equilibrium constants, isotopic equilibrium constants are temperature dependent. Lower temperatures favor greater divergence from unity. As temperature increases, alpha approaches unity (no isotopic fractionation).

When isotope compositions of two compounds, A and B are measured in the laboratory they are expressed by delta (δ) values where the isotopic composition of "A" is expressed as:

$$\delta_A\ ({}^{o}/_{oo}) = \left(\frac{R_A}{R_{STD}} - 1\right) \times 10^3$$

R_{STD} is the defined isotope ratio of a standard sample so that reported values can be compared among different laboratories. Values for δ are reported in per mil enrichment (or depletion if negative) relative to the standard. An example:

$$\delta_A\ ({}^{o}/_{oo}) = \left(\frac{({}^{34}S/{}^{32}S)_{\text{sample A}} - ({}^{34}S/{}^{32}S)_{STD}}{({}^{34}S/{}^{32}S)_{STD}}\right) \times 10^3$$

The measured δ value is related to α by:

$$\alpha_{A-B} = \frac{\delta_A + 1000}{\delta_B + 1000}$$

The fractionation factor for kinetic fractionation processes, sometimes noted as α_k or α^*, may be considered in terms of the ratio of the rate constants for the isotopic substances in a product-forming reaction. For two competing isotopic reactions:

$$A_1 \xrightarrow{k_1} B_1$$

$$A_2 \xrightarrow{k_2} B_2$$

1 = light isotope
2 = heavy isotope
A = reactant
B = product
k = rate constant

the ratio of the rate constants $k_1/k_2 = \alpha^*$. For example,

$$^{32}SO_4 \xrightarrow{k_1} H_2{}^{32}S$$

$$^{34}SO_4 \xrightarrow{k_2} H_2{}^{34}S$$

In most cases k_1 is greater than k_2, because the lighter isotope possesses the smaller bond energy.

Primary Standards

The primary standard for measuring ^{34}S–^{32}S ratios in the laboratory is troilite (FeS) from the Canyon Diablo iron meterorite, and therefore its δ value is zero. Early work by Macnamara and Thode (1951) showed the $^{34}S/^{32}S$ of meteoric sulfur to be remarkably constant ($\pm 0.2°/_{oo}$) and to coincide with the average isotopic value for terrestrial sulfur samples (fig. 1). Meteoritic sulfur provides an ideal standard for comparison of all ^{34}S–^{32}S ratios and is assigned an absolute value of 22.220. Samples more enriched in ^{34}S have positive δ values and those relatively depleted in ^{34}S have negative δ values.

Two internationally accepted standards are used for oxygen isotope ratios: PDB and SMOW (Hoefs, 1980). In this study the ^{18}O standard used is Vienna Standard Mean Ocean Water (V-SMOW) with a given $\delta^{18}O$ of $0.00°/_{oo}$.

Fundamentals of Sulfur Isotope Fractionation

Rates of Approach to Isotopic Equilibrium. Sulfur compounds and the associated oxygen in the sulfate anion have slow rates of approach to isotopic equilibrium in nature. Rates are not only temperature dependent, but may be pH dependent, inasmuch as pH determines the sulfur species through which exchange occurs. Slow reaction rates of low (<250°C) temperatures have made experimentally determined fractionation factors difficult to obtain.

Despite slow sulfur isotope equilibrium establishments, large variations exist in $^{34}S-^{32}S$ isotope ratios between coexisting oxidized and reduced sulfur forms. This variation is mostly due to differences in chemical reaction rates accompanying oxidation or reduction of sulfur compounds; This is classified as kinetic fractionation in bond-breaking reactions.

Physical Fractionation Process. Physical processes account for no appreciable fractionation of sulfur compounds in nature, although they may be significant in a localized situation. Ault and Kulp (1959) concluded that isotopic fractionation in nature is not produced to any large extent by diffusion processes or by transportation and deposition of hydrothermal sulfides. Experiments and field observations by Feely and Kulp (1957) showed that fractionation is negligible ($<\pm 0.1°/_{oo}$) during normal crystallization of $CaSO_4$ from solution. Nriagu (1974) studied sediment absorption of sulfate. He performed experiments using an organic-rich, low-carbonate, clayey mud and 100 ml of a Na_2SO_4 solution of known isotopic composition. Results showed the lighter $^{32}SO_4^{2-}$ was concentrated in the sediment leaving the sulfate in solution enriched in $^{34}SO_4^{2-}$. This effect has been observed in natural environments where aerobic sediments at the mud-water interface are enriched in $^{32}SO_4^{2-}$ relative to dissolved sulfate in the overlying water.

Chemical Fractionation Processes. Two chemical fractionation processes may be involved: sulfur reduction and sulfur oxidation.

1. Sulfur reduction. Sulfur reduction may be inorganic or organic. In inorganic sulfur reduction high temperatures (>250°C) are required to overcome strong bond energies in oxidized sulfur compounds; therefore reactions are restricted to within the earth's crust. Fractionations, reported as δ-value differences, from these high-temperature inorganic processes are in the 25°/oo range (Harrison and Thode, 1957).

Thode, Macnamara, and Collins (1949) first suggested that bacterial sulfate reduction is the most important sulfur fractionating process in the earth's crust. The largest natural sulfur isotope fractionations are due to the sulfate-reducing bacteria Desulfovibrio. These bacteria enzymatically lower the sulfur-oxygen threshold bond energy so reactions can proceed at earth surface temperatures (Pearson and Rightmire, 1980). The most common microbiological reduction is:

$$SO_4^{2-} \rightarrow H_2S$$

The bacteria preferentially reduce the lighter $^{32}SO_4^{2-}$ to produce fractionations ranging from zero to 55°/oo ($\delta_{SO_4} - \delta_{H_2S} = 55°/oo$). Many factors such as metabolic pathways, rates of reduction, and environmental conditions need consideration in predicting bacterial fractionations. Papers discussing experimentally controlled bacterial sulfate reduction include those by Lloyd (1968), Berner (1972), Nielsen (1974), McCready, Kaplan, and Din (1974), and McCready and Krouse (1980). Although extent of fractionation is difficult to predict, laboratory and field data have shown that bacterial reduction somewhat divide sulfur isotopes into an isotopically "heavy" sulfate fraction and an isotopically "light" sulfide mineral fraction.

2. Sulfur oxidation. Ault and Kulp (1959) selected samples to look for isotopic fractionation during surface oxidation of pyrite (FeS_2) to form selenite ($CaSO_4 \cdot 2H_2O$) and found the process to be quantitative, allowing for no isotopic fractionation. In a study to determine origin of dissolved sulfate, Smejkal (1978) studied the oxidative weathering of sulfides and found no major fractionation of sulfur isotopes. Analyses showed a δ value for pyrite to be $+16.4^{\circ}/_{oo}$ and for sulfate, assumed to be a product of weathered pyrite, to be $+15.2^{\circ}/_{oo}$. This apparent lack of fractionation has been helpful in determining sources of sulfate in ground water and springs. For example, sulfate from oxidized sulfide minerals tends to be relatively light compared to sulfate dissolved from evaporite deposits.

Bacterial oxidative fractionation is usually much smaller than bacterial reductive fractionation (Krouse, cited in Fritz and Fontes, 1980). Most commonly oxidation is performed by the genus *Thiobacillus*. Under controlled experiments, it is difficult to delineate chemical and microbiological effects in the reaction. Kaplan and Rittenberg's (1964) experiments showed sulfur isotope fractionation depended on the change in valence and the species formed by the oxidative reaction.

For example, their results, using sulfides and a Thiobacillus culture, showed:

$S^{2-} \xrightarrow[O_2]{} S^{o}$	no fractionation
$S^{2-} \xrightarrow[O_2]{} S_2O_3{}^{2-}$	${}^{34}S_2O_3{}^{2-}$ enriched up to $19^{\circ}/_{\circ\circ}$
$S^{2-} \xrightarrow[O_2]{} SO_4{}^{2-}$	${}^{34}SO_4{}^{2-}$ depleted by $-18^{\circ}/_{\circ\circ}$

Earlier experiments by Nakai and Jensen (1964), using native sulfur and mixed bacterial cultures in wet mud, showed only slight enrichment in the sulfate produced.

Experimental data by Thode, Monster, and Dunford (1961) and field measurements by Holser and Kaplan (1966) showed that when sulfate is precipitated from a solution in the formation of gypsum,

$$Ca^{2+}{}_{(soln)} + SO_4{}^{2-}{}_{(soln)} \rightarrow CaSO_4 \cdot 2H_2O\downarrow$$

the precipitated gypsum is only slightly heavier (1 to $2^{\circ}/_{\circ\circ}$) than the sulfate in brine. This slight fractionation has been neglected in models of oceanic sulfur isotope balance (Holser and Kaplan, 1966; Rees, 1970). The sulfur isotope ratio of marine evaporites, barring any post-depositional alteration, is reflective of the oceanic sulfate isotope at the time of deposition.

Oxygen Isotope Behavior in the Sulfate-Water System

The ${}^{18}O$ isotope, like ${}^{34}S$, can give an indication of the origin and geochemical history of the sulfate ion complex. Extremely slow exchange rates between SO_4^{2-} and H_2O oxygen allow the sulfate anion to retain its memory of the original oxygen of formation.

Exchange between Sulfate and Water. Lloyd (1968) studied oxygen exchange between sulfate and water expressed in the reaction:

$$\tfrac{1}{4}(S^{18}O_4)^{2-} + H_2{}^{16}O \rightleftarrows \tfrac{1}{4}(S^{16}O_4)^{2-} + H_2{}^{18}O$$

He calculated the rate of oxygen exchange in ocean water at pH 8.2 and T = 4°C, expressed in half-time ($t_{\frac{1}{2}}$), as 50,000 years. Hoering and Kennedy (1957) studied the reaction kinetics and found the rate to be a function of temperature, pH, and H_2SO_4 activity. In laboratory experiments, exchange is mediated by lowering the pH to less than 2. Under these conditions the actual isotopic exchange occurs with the bisulfate (HSO_4^-) ion and results cannot be extrapolated to equilibrium values for the sulfate (SO_4^{2-}) ion. Radmer (1972) also confirmed that sulfate and water oxygen undergo virtually no exchange except by the mechanism of acid-catalyzed dehydration. His exchange experiments in a neutral 0.1 M Na_2SO_4 solution indicated longer exchange half-life than predicted by Lloyd (1968) and Longinelli and Craig (1967).

Holser and others (1979) proposed a model for the sulfate-^{18}O balance maintained in sea water. In order for ocean-water sulfate oxygen to remain at a value of 8.6°/₀₀ he developed a sulfate flux balance and proposed even slower exchange rates than those predicted by experiments. Zak, Sakai, and Kaplan (1980) corroborated Holser and others' (1979) results by investigating sulfate isotopes in deep-sea core interstitial waters, finding a nearly constant $\delta^{18}O$ (SO_4^{2-}) value for a period of about 50 million years. They deduced that the $t_{\frac{1}{2}}$ for ocean sulfate-water exchange is greater than 5×10^9, five orders of magnitude greater than Lloyd's predicted value. The isotopic stability and constancy of oceanic sulfate have provided a tool for studying the geochemical sulfur cycle in both present and past oceans using age-correlated evaporite deposits (Claypool and others, 1980).

Several field studies of dissolved sulfate, both of sedimentary sulfide and evaporite origin and likely unaffected by bacterial action, have shown no correlation between dissolved sulfate and water $\delta^{18}O$ (Schwarcz and Cortecci, 1974; Longinelli, 1968) demonstrating absence of isotopic exchange.

Exchange between Anhydrite and Water. ^{18}O analyses of oxygen-bearing mineral–water systems have been a tool in deciphering past geologic environments. Mineral groups like carbonates, silicates, and oxides have been used to indicate temperatures at the time of formation. Due to slow sulfate-water oxygen exchange in normal near-surface geologic environments, the $\delta^{18}O$ of sulfate should reflect long-term average environmental conditions rather than instantaneous conditions as reflected in carbonate ^{18}O studies.

Lloyd's (1967, 1968) experiments established a temperature vs. α relationship for the anydrite-water ($CaSO_4$–H_2O) system in the temperature range 100°C to 500°C (table 2). The curve is similar to that of other water-mineral systems, but the slope is greater, thus fractionation effect is larger. Anhydrite in the $CaSO_4$–H_2O system enriches ^{18}O by about 2°/oo at 25°C (Lloyd, 1968). Friedman and

Table 2. Sulfate mineral equilibrium fractionation factors

Fractionation Factor	Reference
$\ln \alpha_{CaSO_4-H_2O} = (3878/(T^2) - 0.0034$	Lloyd (1968)
$\ln \alpha_{BaSO_4-H_2O} = (3000/(T^2) - 0.00679$	Friedman and O'Neil (1977)
$\ln \alpha_{CaSO_4-H_2O} = (3210/(T^2) - 4.72$	Hitoshi and others (1981)

O'Neil (1977) published data from Robinson and Kusakabe for fractionation in the barite ($BaSO_4$)-water system (Table 2).

Gypsum, a hydrated sulfate mineral ($CaSO_4 \cdot 2H_2O$), is normally deposited before anhydrite in a marine evaporite facies. Fontes (1965) found the water of hydration in gypsum enriched by 3 to 4 per mil in ^{18}O compared to water in which the gypsum is in equilibrium. Holser and others (1979) found this water of crystallization and hydration to be 3.2 to 12.0 per mil more enriched in ^{18}O than in the solution water. Their paper discusses synsedimentary and postdepositional processes such as exchange with ^{18}O (SO_4^{2-}) and exchange with ^{18}O (H_2O) of the subsurface that could alter $\delta^{18}O$ in sulfate minerals. They concluded that the ^{18}O (sulfate minerals) are neither in equilibrium with the water of hydration nor with the formation waters. Zak and others (1980) reached the same conclusion from supportive evidence of constant $\delta^{18}O$ values and sulfate concentrations for a 50-million-year time span in interstitial waters of deep-sea drill cores.

Evidence does exist that some exchange may occur between sulfate minerals and formation or hydration water. Cortecci and others

(1981) reported that anhydrite in cores from the Burano Formation showed a range of 7.5 percent in $\delta^{18}O$ (SO_4^{2-}) values and suggested that postdepositional exchange could account for this wide range in values from the same formation.

Recent fractionation factors in the anhydrite–water system (Hitoshi and others, 1981) are smaller than those reported by Lloyd (1969) at any temperature (table 2). Exchange rates varied greatly with changes in pH and the sulfate mineral involved. For example, barium sulfate exchanged more quickly than calcium sulfate, although the former was less soluble under the experimental conditions. Hitoshi and others (1981) proposed that the exchange mechanism may be dissolution and recrystallization, whereby the acid solution would increase the rate of incorporation of sulfate ions into the solid phase. The barite–water and anhydrite–water experimental data plotted as almost parallel lines with ^{18}O more enriched in anhydrite by 2 per mil at each temperature due to stronger "force constants" in the calcium-to-sulfate-bonded tetrahedron.

Precipitation of Gypsum and Anhydrite. Evaporation of a saturated calcium sulfate ($CaSO_4$) solution precipitated gypsum ($CaSO_4 \cdot 2H_2O$) that concentrated ^{18}O (SO_4) by about 2 per mil relative to the ^{18}O ($SO_4{}^{2-}{}_{soln}$) (Lloyd, 1968). Evaporation pan experiments showed the gypsum to be enriched by about 3.6 per mil, but whether the fractionation is a kinetic or an equilibrium effect remains unknown. Experiments by Holser and others (1979), who evaluated ^{18}O isotope fractionation in crystallization of gypsum, gave a "best value" for $\Delta^{18}O$

$(CaSO_4)/\Delta^{18}O\ (SO_4{}^{2-}{}_{soln}) = 3.6\%$. Using sulfate oxygen isotope data to construct marine evaporite age curves (Claypool and others, 1980) assumed a $\Delta^{18}O$ (crystallization) equal to $3.6^{\circ}/_{oo}$, based on Lloyd's (1968) work. Marine evaporites were presumed to be deposited with this consistent $3.6^{\circ}/_{oo}$ $^{18}O\ (SO_4)$ enrichment and to remain unaffected by repeated crystallizations.

Field data from Cortecci and others (1981) showed a $^{18}O(SO_4)^{2-}$ fractionation of about $3^{\circ}/_{oo}$ for evaporite deposition. Massive selenite–gypsum beds believed to have precipitated from evaporating sea-water bodies showed a $3^{\circ}/_{oo}$ enrichment over the $^{18}O(SO_4)^{2-}$ dissolved in sea water.

Bacterial Reduction of Sulfate. No definitive measurement of oxygen fractionation by bacteria has been made in a natural system (Holser and others, 1979). The $\Delta^{18}O\ (SO_4)$ fractionation has been estimated by taking the ratio of $\Delta^{18}O/\Delta^{34}S$ in laboratory experiments and multiplying by the fractionation of sulfur $(\Delta^{34}S)$ in the natural system. Laboratory experiments (Lloyd, 1967) showed that bacteria favor the lighter ^{16}O, leaving the residual dissolved sulfate enriched in ^{18}O. Both pure and natural mixed cultures showed a "best" kinetic fractionation factor (α^*) of -4.6 per mil. Because values for α were known to be variable, depending on experimental conditions, ensuing work by Mizutani and Rafter (1969, 1973) and Rafter amd Mizutani (1967) focused on $\Delta^{18}O/\Delta^{34}S$ correlations in natural systems and laboratory experiments. Their work at Lake Vanda, Antarctica (1967) and in laboratory experiments (1969) displayed an enrichment ratio equal to 1/4 in which the ^{34}S is 4 times more enriched than the ^{18}O in the residual dissolved sulfate. The ^{18}O value of residual sulfate was later found by Mizutani and Rafter (1973) to depend on the ^{18}O (H_2O) in which the sulfate was formed. The proposed explanation was sulfate–water oxygen exchange through intermediates in the enzymatic bacterial reduction of sulfate to sulfide:

$$2CH_2O + SO_4^{2-} = H_2O + CO_2 + HCO_3^- + HS^-$$

If this mechanism is operable, then the ratio of $\Delta^{18}O/\Delta^{34}S$ enrichment in remaining sulfate must be variable, depending on the ^{18}O (H_2O) and water–sulfate oxygen exchange.

Bacterial Oxidation of Sulfur Species. The ^{18}O value of sulfate produced from bacterial oxidation is incorporated into the sulfate ion from two sources: the water molecule and the dissolved atmospheric oxygen. Lloyd (1967) proposed that their proportions were 68 percent from water and 32 percent from dissolved oxygen, based on some experimental mass balances. His model assumed that fractionation occurred only in the incorporation of dissolved oxygen into the sulfate. Mizutani and Rafter (1969) found the small isotopic fractionation during bacterial oxidation of sulfur to reflect mainly the ^{18}O of the water. Cortecci (1973) pointed out that the isotopic value of dissolved oxygen is a function of biological activity therefore making predictions based on Lloyd's model more uncertain.

Inorganic Oxidation of Sulfide. Inorganic sulfide weathering plays a minor part in the sulfur cycle compared to bacterial oxidation of sulfide (Holser and others, 1979). Because sulfides such as pyrite are among the most abundant minerals in a uranium roll-type deposit (Warren, 1972), inorganic oxidation received attention in this study. Considerable opportunity exists for inorganic sulfide oxidation in both mining of the ore and extraction of the uranium.

Similar to bacterial sulfide oxidation, prediction of the $\delta^{18}O$ of sulfate generated from sulfides is difficult. Part of the sulfate oxygen originates from the water molecule and part from dissolved molecular oxygen. The sulfide-to-sulfate oxidative reaction occurs in a series of poorly understood steps whereby some of the intermediate sulfur-oxy species such as SO_3^{2-} could exchange with water at considerable rates (Schwarcz and Cortecci, 1974). Lloyd (1967, 1968) experimented with oxidation in a sodium sulfide solution and proposed a two-step reaction:

1. $S^{2-} + H_2O + O_2 \rightleftarrows SO_3^{2-}$ rapid
2. $SO_3^{2-} + \frac{1}{2}O_2 \rightleftarrows SO_4^{2-}$ slow

An 8.7 per mil fractionation occurs in the incorporation of molecular oxygen in step (1):

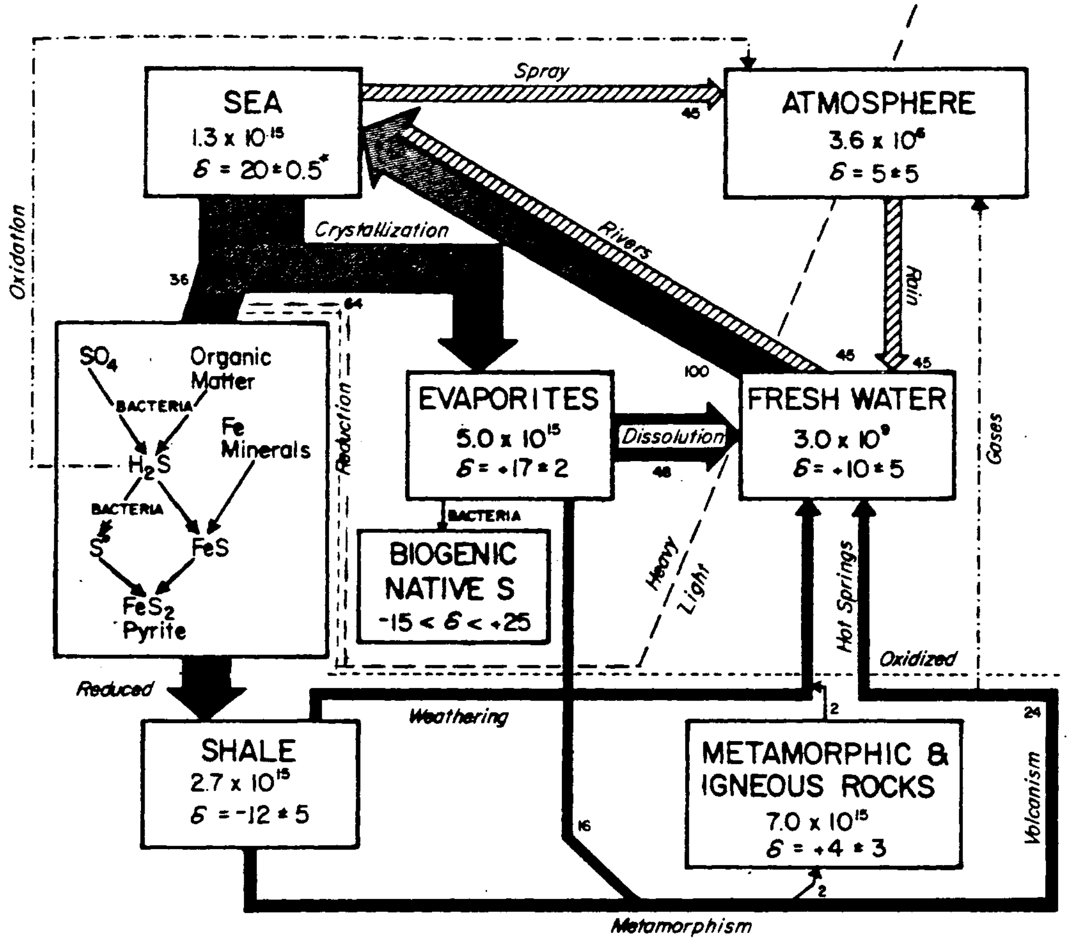
$$\alpha_{\text{experimental}} = \frac{\text{rate } ^{18}\text{O consumed}}{\text{rate } ^{16}\text{O consumed}} \cong -8.7^{\circ}/_{oo}$$

From the steady-state isotopic composition of oceanic sulfate, Lloyd (1967) estimated the relative proportions of sulfate oxygen to be 0.68 from H_2O and 0.32 from O_2. Most investigators for lack of more quantitative experimental data have used Lloyd's (1968) model to predict $\delta^{18}O$ (SO_4^{2-}) from sulfide oxidation.

Longinelli and Craig (1967) and Smejkal (1978) looked at $\delta^{18}O$ from sulfates speculated to be derived from sulfide oxidation. Their results were juxtaposed. Smejkal found the lightest sulfate $\delta^{18}O$ values (-2°/₀₀ to -6°/₀₀) in descending mine waters where sedimentary pyrite oxidation was apparent. Longinelli and Craig found sulfates in saline lakes believed to have originated from oxidation of igneous sulfides to have ^{18}O (SO_4^{2-}) values up to 23°/₀₀, near that of atmospheric oxygen. However, it is unknown whether oxidation was bacterially mediated. Using observed $\delta^{18}O$ (H_2O) from where the sulfates were precipitated and assuming $\delta^{18}O$ (O_2) of air equal to 23 per mil, Zak and others (1980) compared $\delta^{18}O$ (SO_4^{2-}) formed by surficial oxidation of pyrite and volcanic hydrogen sulfide to Lloyd's predictive model. They found no agreement between values. A better defined concept of the sulfide oxidation kinetics is needed before prediction of oxygen isotope effects during sulfide oxidation can be made.

Distribution of Sulfur and Associated Oxygen Isotopes in Nature

The fractionation mechanisms outlined above have selectively distributed the sulfur, and to a lesser extent the oxygen, isotopes between the major sulfur reservoirs on earth. Figure 1 shows the range in sulfur isotopic composition of each reservoir, and figure 2 flow charts the geochemical cycling of sulfur between reservoirs. Average isotopic values and estimated mass of sulfur in each reservoir are indicated. Figure 1 shows that the largest isotopic differences on a global scale are found within both the freshwater sulfate and the sedimentary rock sulfide that constitute the reservoirs of interest in this


SEA
1.3 x 10^{15}
δ = 20 ± 0.5*
Spray
45
ATMOSPHERE
3.6 x 10^{6}
δ = 5 ± 5
Crystallization
Rivers
Rain
Oxidation
36
64
SO$_4$
Organic Matter
BACTERIA
Fe Minerals
H$_2$S
BACTERIA
S
FeS
FeS$_2$
Pyrite
Reduction
100
45
45
EVAPORITES
5.0 x 10^{15}
δ = +17 ± 2
Dissolution
48
FRESH WATER
3.0 x 10^{9}
δ = +10 ± 5
Gases
BACTERIA
BIOGENIC NATIVE S
-15 < δ < +25
Heavy
Light
Hot Springs
Oxidized
Reduced
Weathering
2
24
SHALE
2.7 x 10^{15}
δ = -12 ± 5
METAMORPHIC & IGNEOUS ROCKS
7.0 x 10^{15}
δ = +4 ± 3
Volcanism
16
2
Metamorphism

Masses of sulfur in metric tons and mean δ are shown for each reservoir (* = Since Late Cretaceous).

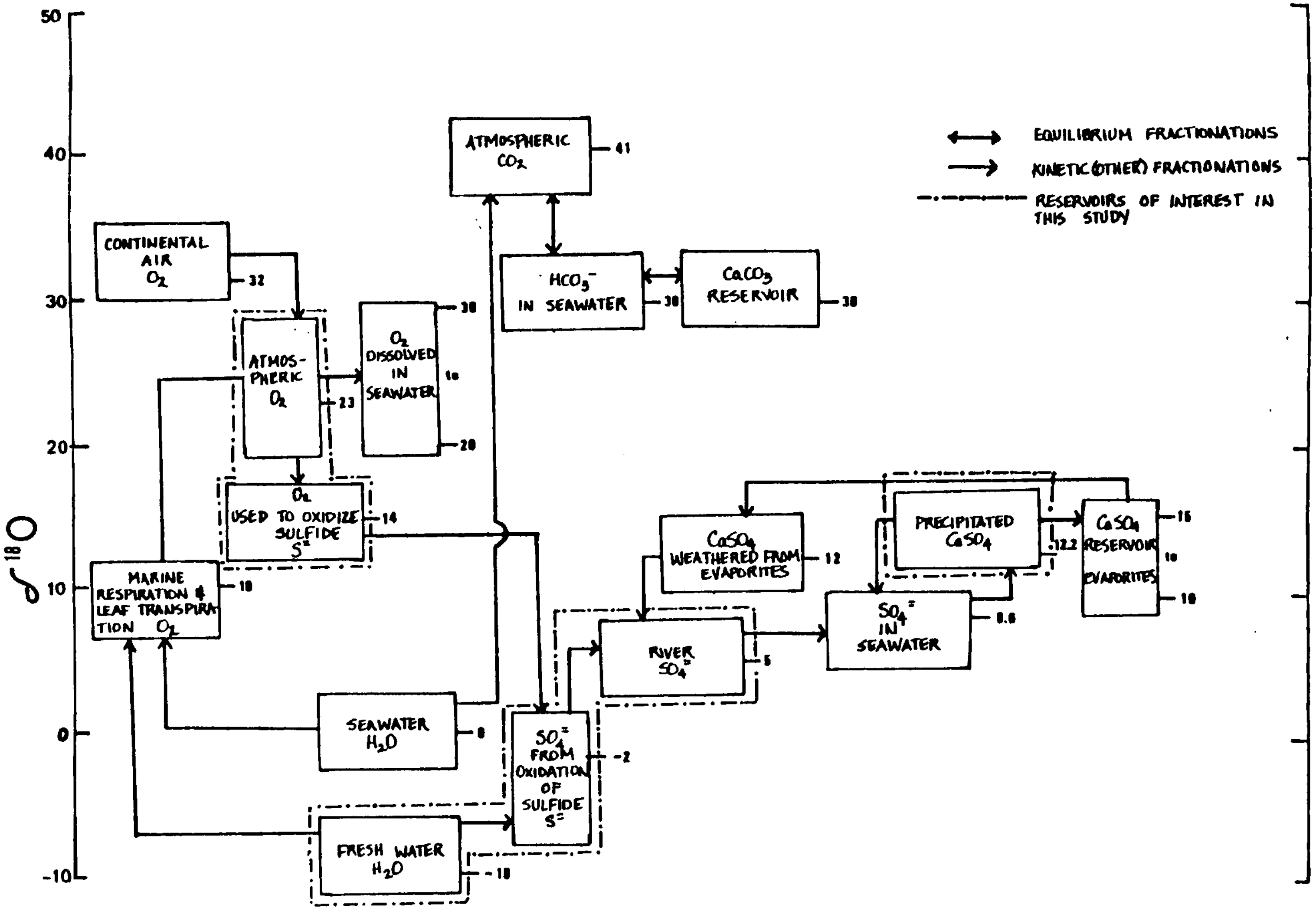
— — — Above this line heavy (δ > + 10 ‰) sulfur predominates, and below it light (δ < + 10‰) sulfur predominates.

------- Material above this line is oxidized, and below it, reduced.

Long-term (➡) and short-term (⇨) fluxes of sulfur between reservoirs are indicated on the basis of 100 for long-term flux of fresh-water sulfate to the sea.

Figure 2. Geochemical sulfur cycle. -- Data from Holser and Kaplan (1966).

ground-water study. However, at a given location such as the Kerr-McGee uranium millsite, each reservoir may have a distinct and fairly constant sulfur or oxygen, or both, isotopic composition. Holser and others (1979) presented a critical evaluation of the isotopic geochemistry of oxygen that influences the sulfur cycle. Figure 3, adapted from their study, is a diagrammatic flowsheet of oxygen isotopes showing relations among $\delta^{18}O$ values in various reservoirs influencing sulfate isotopic composition. The reliability of isotopic values and uncertainties of fractionations are discussed within the paper. Dotted lines indicate the reservoirs of most interest to this study. Generally, unlike the sulfur cycle (fig. 2), sulfate reservoirs received oxygen inputs from at least two isotopically different oxygen sources, thus multiplying the uncertainty in predicting sulfate ^{18}O values. The redeeming feature of $\delta^{18}O$ (SO_4) is its tendency to remain unchanged once the mineral or dissolved sulfate is formed. In this manner the oxygen isotopic label on the sulfate may provide a stable tracer as well as give some indication of the geochemical history of the sulfate ion.



$\delta^{18}O$
50
40
30
20
10
0
-10
ATMOSPHERIC CO_2
41
CONTINENTAL AIR O_2
32
ATMOS-PHERIC O_2
23
O_2 DISSOLVED IN SEAWATER
30
10
20
O_2 USED TO OXIDIZE SULFIDE $S^=$
14
MARINE RESPIRATION & LEAF TRANSPIRATION O_2
10
SEAWATER H_2O
0
FRESH WATER H_2O
-10
HCO_3^- IN SEAWATER
30
$CaCO_3$ RESERVOIR
30
$SO_4^=$ FROM OXIDATION OF SULFIDE $S^=$
-2
RIVER $SO_4^=$
5
$CaSO_4$ WEATHERED FROM EVAPORITES
12
$SO_4^=$ IN SEAWATER
8.6
PRECIPITATED $CaSO_4$
12.2
$CaSO_4$ RESERVOIR EVAPORITES
15
10
10
EQUILIBRIUM FRACTIONATIONS
KINETIC (OTHER) FRACTIONATIONS
RESERVOIRS OF INTEREST IN THIS STUDY

Figure 3. Oxygen isotope geochemistry

CHAPTER 3

SITE DESCRIPTION

Interpretation of any tracer study requires an understanding of the hydrologic system through which a tracer travels. The following sections provide a concise description of the geographic, geologic, and hydrologic setting of the Kerr-McGee mining and milling operation. Mining and milling practices are described with regard to their usage, chemical alteration, and disposal of water at the site. Present hydrologic conditions in the alluvium and Tres Hermanos Sandstone Member are then addressed, showing responses of the hydrologic system to mining and milling.

Location of Study Area

The Kerr-McGee Ambrosia Lake mining and milling complex is in the Grants Mineral Belt in the southeastern corner of McKinley County, New Mexico (fig. 4). Kerr-McGee's millsite in sec. 31, T. 14 N., R. 9 W. is the focal point of this study. Mines that supply ore to the mill are east, north, and northwest in secs. 17, 19, 22, 24, 30, and 33. Locations of the mill and adjacent ponds are shown in figure 5; dashed lines delineate the approximate area of subsurface mining.

The Kerr-McGee complex lies in the Ambrosia Lake valley between two escarpments trending northwest (fig. 4). Mesa Montañosa to the south is composed of the Morrison Formation capped by Dakota Sandstone. The northern escarpment, San Mateo Mesa, is composed of

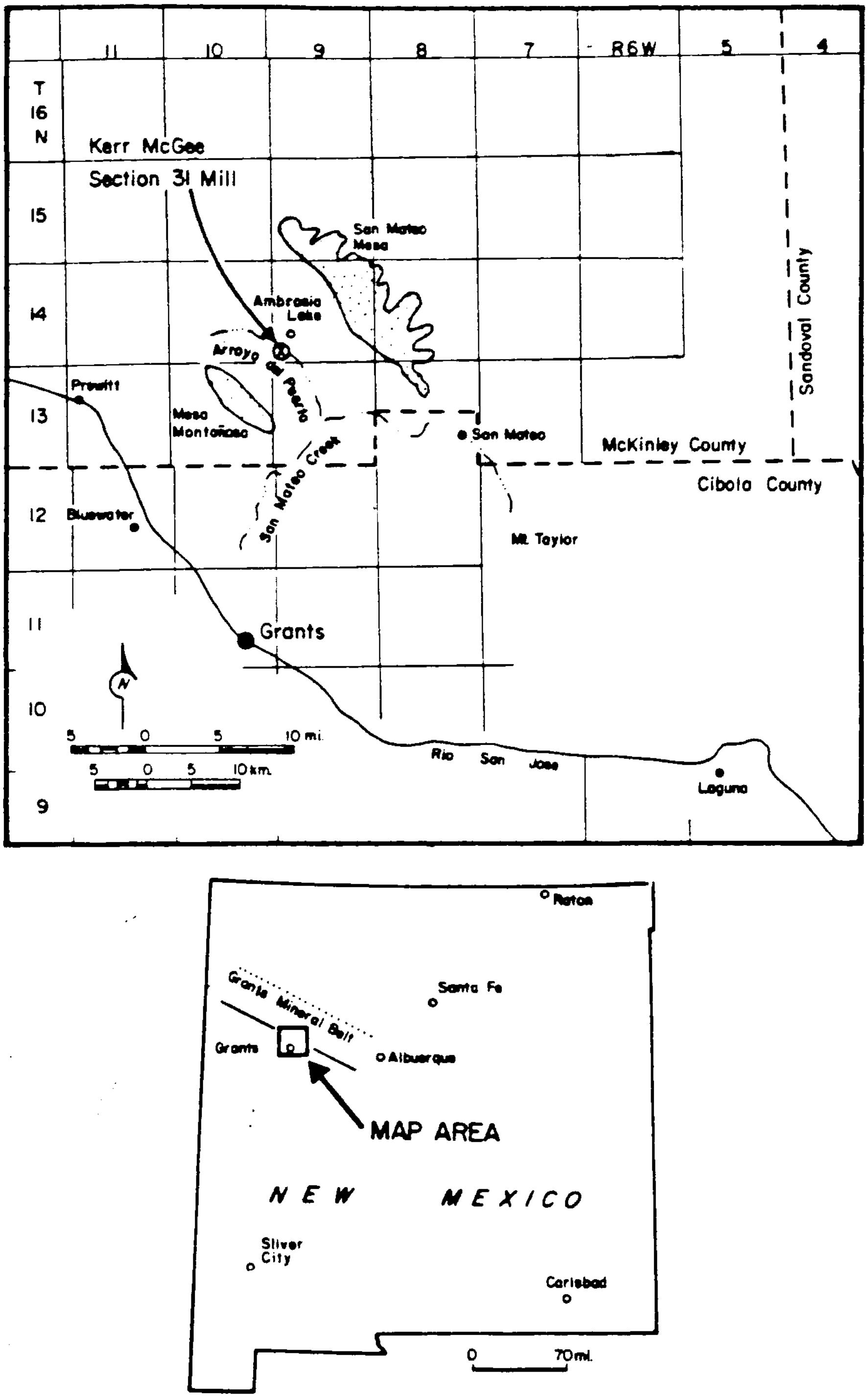

11
10
9
8
7
R6W
5
4
T 16 N
15
14
13
12
11
10
9
Kerr McGee Section 31 Mill
San Mateo Mesa
Ambrosia Lake
Arroyo del Puerto
Prewitt
Mesa Montañosa
San Mateo Creek
San Mateo
Sandoval County
McKinley County
Cibola County
Bluewater
Mt. Taylor
Grants
N
5 0 5 10 mi.
5 0 5 10km.
Rio San Jose
Laguna
Raton
Santa Fe
Grants Mineral Belt
Grants
Albuquerque
MAP AREA
NEW MEXICO
Silver City
Carlsbad
0 70mi.

Figure 4. Location map of study area

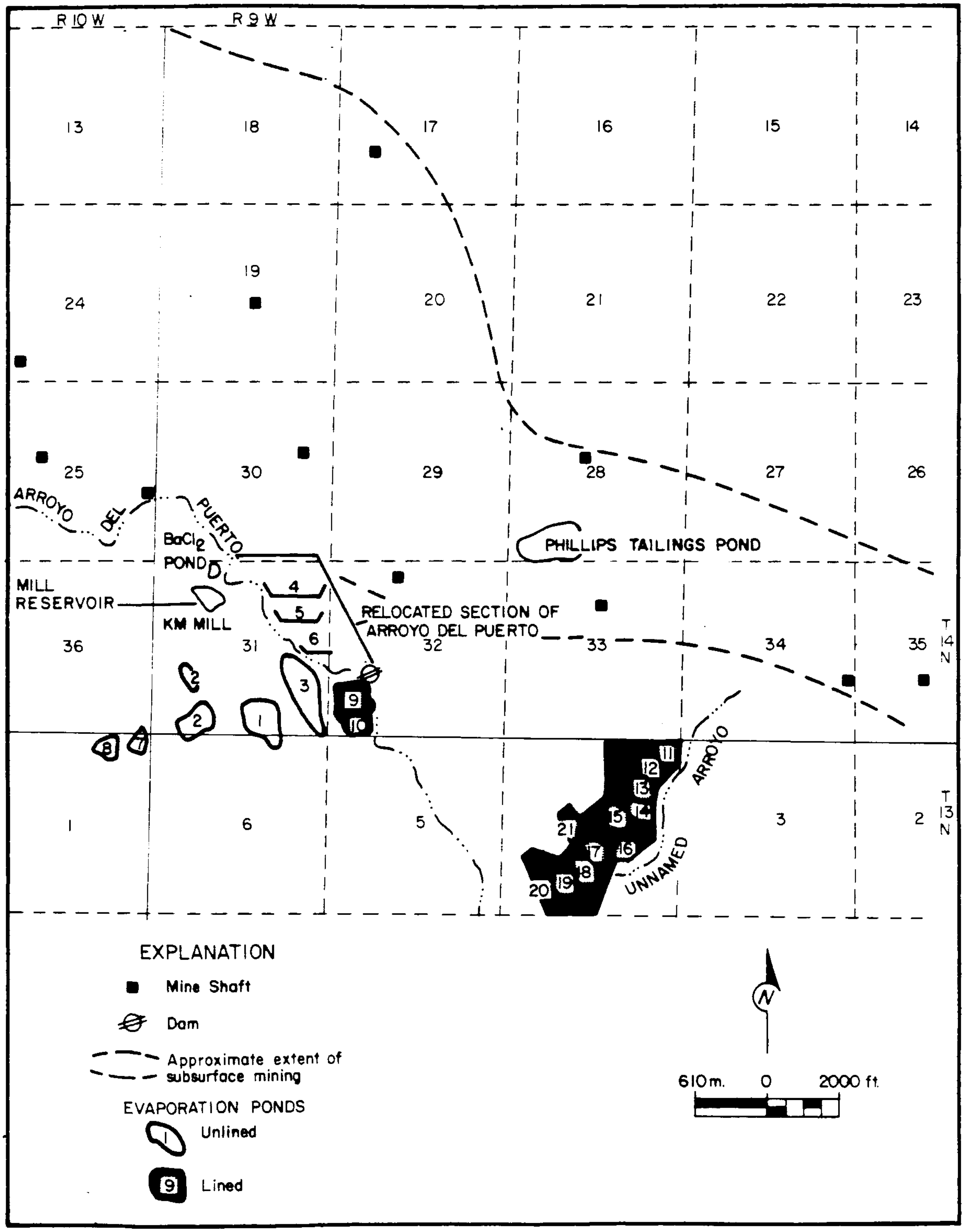

R 10 W
R 9 W
13
18
17
16
15
14
19
24
20
21
22
23
25
30
29
28
27
26
ARROYO DEL PUERTO
BaCl2 POND
PHILLIPS TAILINGS POND
MILL RESERVOIR
KM MILL
RELOCATED SECTION OF ARROYO DEL PUERTO
36
31
32
33
34
35
T 14 N
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
ARROYO
UNNAMED
T 13 N
EXPLANATION
Mine Shaft
Dam
Approximate extent of subsurface mining
EVAPORATION PONDS
Unlined
Lined
N
610m.
0
2000 ft.

Figure 5. Map of Kerr-McGee section 31 millsite

the younger Mesaverde Group and is capped by Point Lookout Sandstone. The valley is drained by Arroyo del Puerto, which originates northwest of Kerr-McGee's operation (fig. 4). Arroyo del Puerto has been perennial since the 1950s when mine dewatering operations began discharging waters into its course. Arroyo del Puerto joins San Mateo Creek 4 miles south of the millsite. San Mateo Creek disappears in sec. 1 or 12, T. 13 N., R. 10 W., indicating recharge to the alluvial aquifer, then subsurface flow travels southeast toward the Rio San Jose (Nylander, 1979; Brod, 1980). Ambrosia Lake is a natural depression, normally dry, which contains water only after heavy rains.

Geohydrology

The following geohydrologic description of Kerr-McGee's section 31 millsite focuses upon the alluvial aquifer and Tres Hermanos sands of the Mancos Shale from which water samples were collected. Other geologic formations are discussed mainly with respect to their influence on quantity or quality of water in the alluvial aquifer due to mine dewatering discharges. Information presented in the following sections on hydrogeology, flow regime in alluvium, and water balance at the millsite is abstracted from Ganus's (1980) detailed study of the site, except where noted.

Structure

The Kerr-McGee millsite is on the southern edge of the San Juan Basin. The Zuni uplift to the southwest is the predominant structural feature of the area. This uplift flexed Triassic-to-Cretaceous sedimentary rocks, which form the basin fill, so that these units now have a north-to-northeastern regional dip of 1 to 3 degrees. Postdepositional periods of tectonic activity have produced faults and fractures with a predominantly northern trend. Block faulting is recognized in the area; the millsite is on a horst bounded by two faults 4 miles to the east and west of the mill. Older faults in the area are partially healed and may retard ground-water flow, whereas younger faults increase the rate of ground-water flow. Some shaly layers between aquifers contain significant bentonitic material; where these layers are fractured they are generally closed and do not permit interaquifer communication.

Figure 6, adapted from Kelly, Link, and Schipper (1980), is a geologic map of pre-Quaternary geology of the Ambrosia Lake area. The cross section shown in figure 7, adapted from Brod (1980), is 0.75 miles southeast of the millsite. The millsite is in the Arroyo del Puerto alluvial valley resting on Mancos Shale between more resistant sandstone mesas. Younger rock units outcrop as cliffs northeast of the mill on San Mateo Mesa and older units outcrop south of the site on Mesa Montañosa. A stratigraphic column for the Ambrosia Lake area is also shown in figure 7 to indicate thicknesses of each formation.

Stratigraphy

Uranium ore is mined from the Westwater Canyon Member of the Morrison Formation. Because mining activity does not ordinarily penetrate a significant distance below this horizon, the following discussion is limited to those units between ground surface and the Morrison Formation. Formations are presented in order from oldest to youngest.

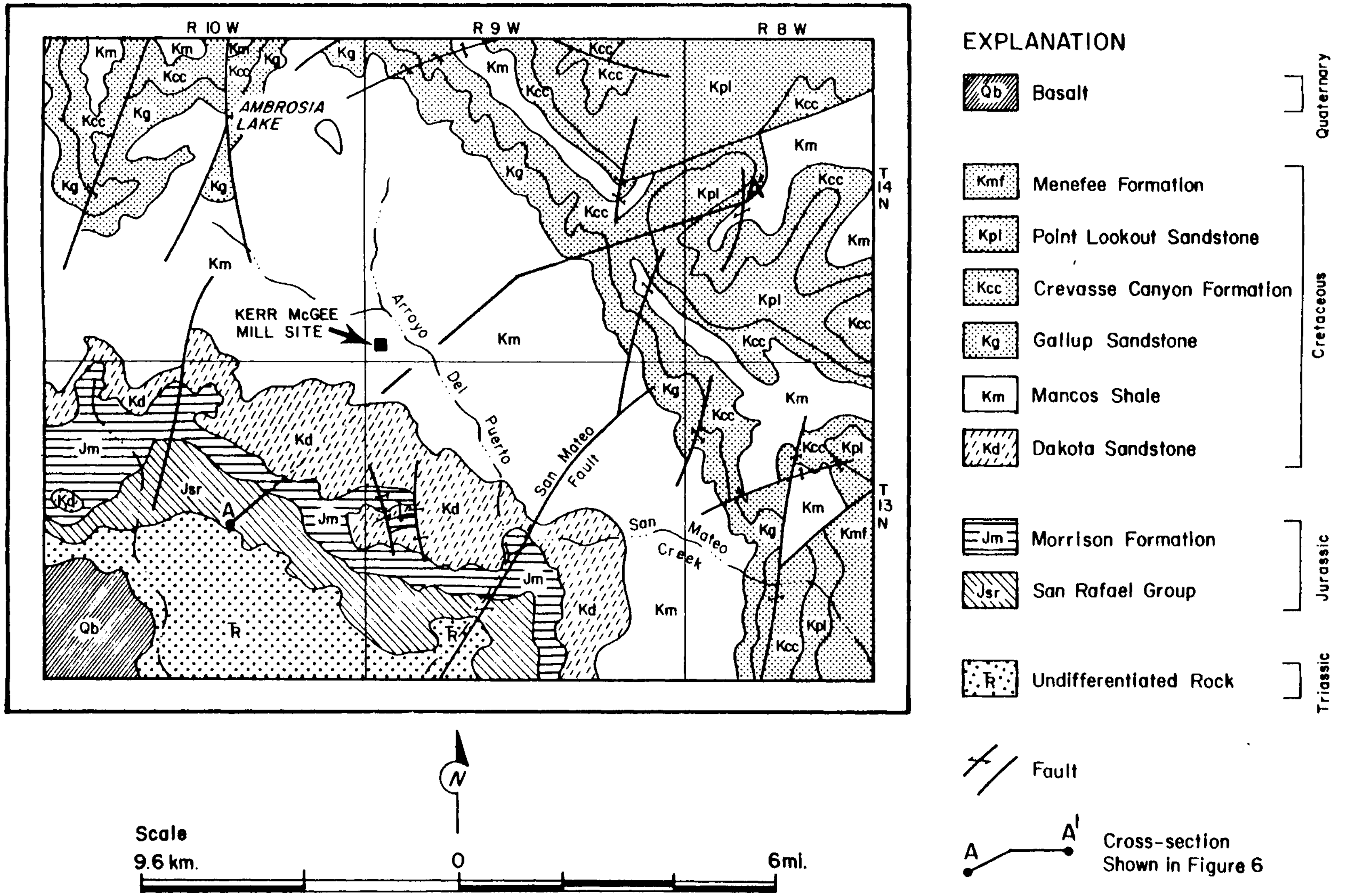

R 10 W
R 9 W
R 8 W
T 14 N
T 13 N
AMBROSIA LAKE
KERR McGEE MILL SITE
Arroyo Del Puerto
San Mateo Fault
San Mateo Creek
Km
Kcc
Kg
Kpl
Kmf
Kd
Jm
Jsr
TR
Qb
A
N
Scale
9.6 km.
0
6mi.
EXPLANATION
Qb Basalt
Kmf Menefee Formation
Kpl Point Lookout Sandstone
Kcc Crevasse Canyon Formation
Kg Gallup Sandstone
Km Mancos Shale
Kd Dakota Sandstone
Jm Morrison Formation
Jsr San Rafael Group
TR Undifferentiated Rock
Quaternary
Cretaceous
Jurassic
Triassic
Fault
A A' Cross-section Shown in Figure 6

Figure 6. Geologic map of Ambrosia Lake area. -- Adapted from Kelly, Link, and Schipper (1980)

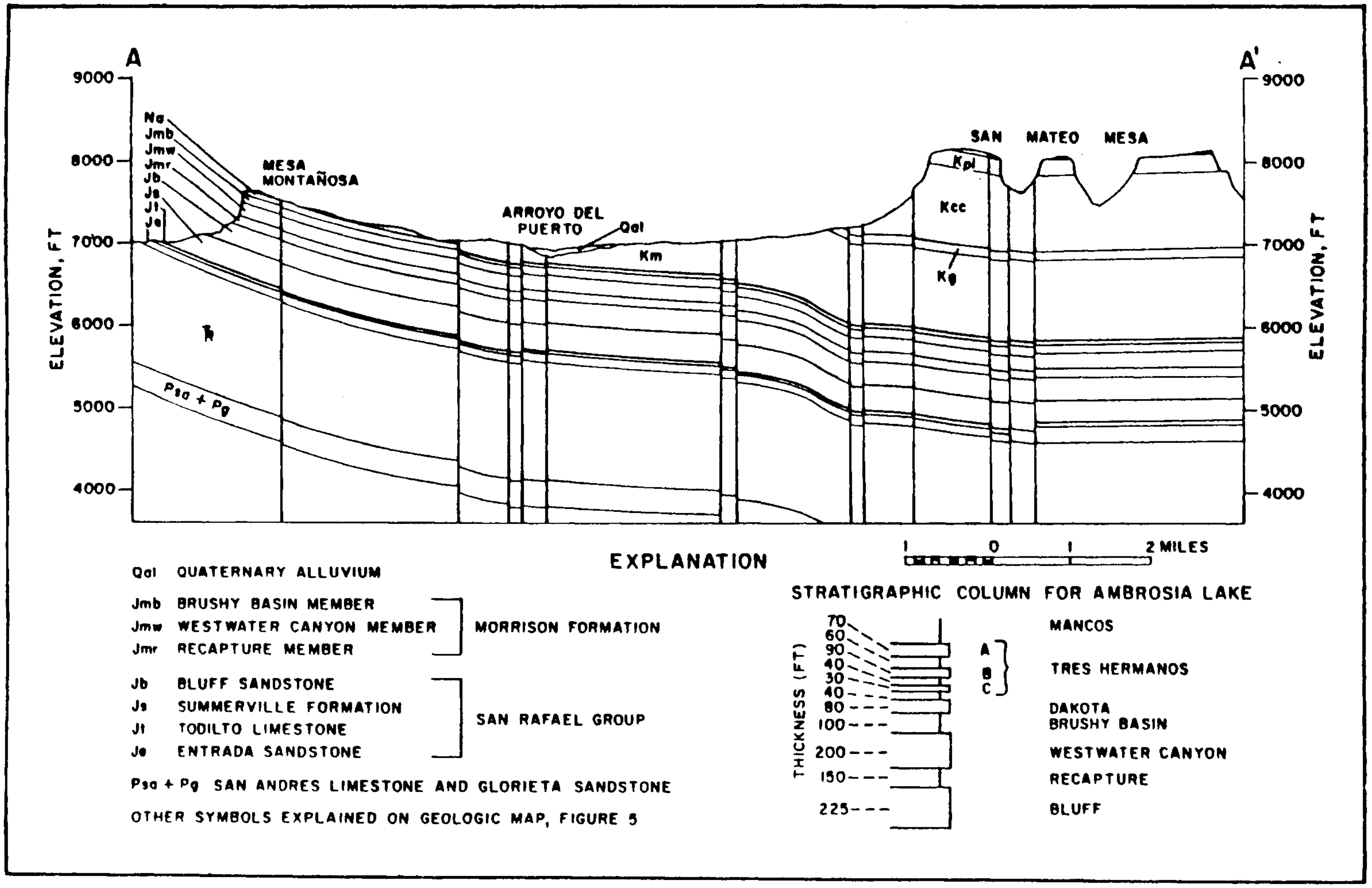

A
A'
9000
8000
7000
6000
5000
4000
ELEVATION, FT
Na
Jmb
Jmw
Jmr
Jb
Js
Jt
Je
MESA MONTAÑOSA
ARROYO DEL PUERTO
Qal
Km
SAN MATEO MESA
Kpl
Kcc
Kg
Psa + Pg
1 0 1 2 MILES
EXPLANATION
Qal QUATERNARY ALLUVIUM
Jmb BRUSHY BASIN MEMBER
Jmw WESTWATER CANYON MEMBER
Jmr RECAPTURE MEMBER
MORRISON FORMATION
Jb BLUFF SANDSTONE
Js SUMMERVILLE FORMATION
Jt TODILTO LIMESTONE
Je ENTRADA SANDSTONE
SAN RAFAEL GROUP
Psa + Pg SAN ANDRES LIMESTONE AND GLORIETA SANDSTONE
OTHER SYMBOLS EXPLAINED ON GEOLOGIC MAP, FIGURE 5
STRATIGRAPHIC COLUMN FOR AMBROSIA LAKE
THICKNESS (FT)
70
60
90
40
30
40
80
100
200
150
225
A
B
C
MANCOS
TRES HERMANOS
DAKOTA
BRUSHY BASIN
WESTWATER CANYON
RECAPTURE
BLUFF

Figure 7. Cross section showing stratigraphy of the Ambrosia Lake area. -- Adapted from Brod (1980).

Morrison Formation. The Morrison Formation, a continental and lacustrine deposit, comprises three members: the Recapture, Westwater Canyon, and Brushy Basin. The Recapture Member is composed of intrastratified siltstone, shale, and fine sandstone. In the Ambrosia Lake area it is about 100 feet (30.5 m) thick and low in permeability, effectively confining the Westwater Canyon aquifer from the underlying Bluff Sandstone.

The Westwater Canyon Member contains the trends of uranium ore and is a significant aquifer, which yields water of high quality. Coefficients of transmissivity are in the range of 100-200 ft^2/day (Kelly and others, 1980). The Westwater is composed of fine- to coarse-grained, poorly sorted arkosic sand typical of fluvial deposits with cut-and-fill structures, crossbedding, and abrupt changes in grain size. Early data indicate that prior to mining, the Westwater potentiometric surface was between 6,500 and 6,600 ft and that water quality was very good. The Westwater Canyon Member is approximately 200 ft (70 m) thick in the study area.

The Brushy Basin Member comprises 100 ft (30.5 m) of bentonitic mudstones and thin sandstone lenses, which conform and intertongue with the upper Westwater. This unit acts as an effective aquitard overlying the Westwater Canyon aquifer. Uncased wells left open in the unit quickly seal due to expansion of the clay.

Dakota Sandstone. The Dakota Sandstone is a fine-grained, clean sandstone with fair to good permeability. Historical data indicate that its premining potentiometric surface was close to or slightly above that of the Westwater Canyon aquifer, approximately 6,000 feet. The Dakota is about 80 ft (24 m) thick in the study area. The water quality is quite variable shown by total dissolved solids (TDS) ranging from 400 to 1,500 mg/L derived from specific conductance measurements.

Mancos Shale and Tres Hermanos Sandstone Member. The Mancos Shale forms the valley floor at Ambrosia Lake and contains several local sandstone lenses identified as the Tres Hermanos Sandstone Member. The sandstone lenses are referred to as A, B, and C, from lowest to highest. Tres Hermanos sandstones cap most low hills around the millsite. Much of the rock has become deeply weathered and is mapped as saprolite. Due to weathering the Tres Hermanos is often difficult to distinguish from overlying alluvium. Figure 8 shows outcrops of the Tres Hermanos and saprolite in the millsite area. Sparse information describing the saturated state of the Tres Hermanos prior to mining is available. East of the mill high yields from these sandstones are reported. Cooper and John (1968, p. 39) reported that the "middle sandstone bed of Mancos" yielded 900 and 200 gpm to two mines in the San Mateo Mesa area, and Brod (1980) reported that the Tres Hermanos is very productive at the Mt. Taylor mine (10 miles, 16 km) to the east. A well in section 31 completed in Tres Hermanos-B was artesian when drilled in 1977.

Alluvium. The valley is filled with 90 to 100 ft (27.4 to 30.5 m) of eolian and fluvial material derived from the shale and sandstone. Figure 9 is an isopach map of the alluvial deposit. Well logs show that

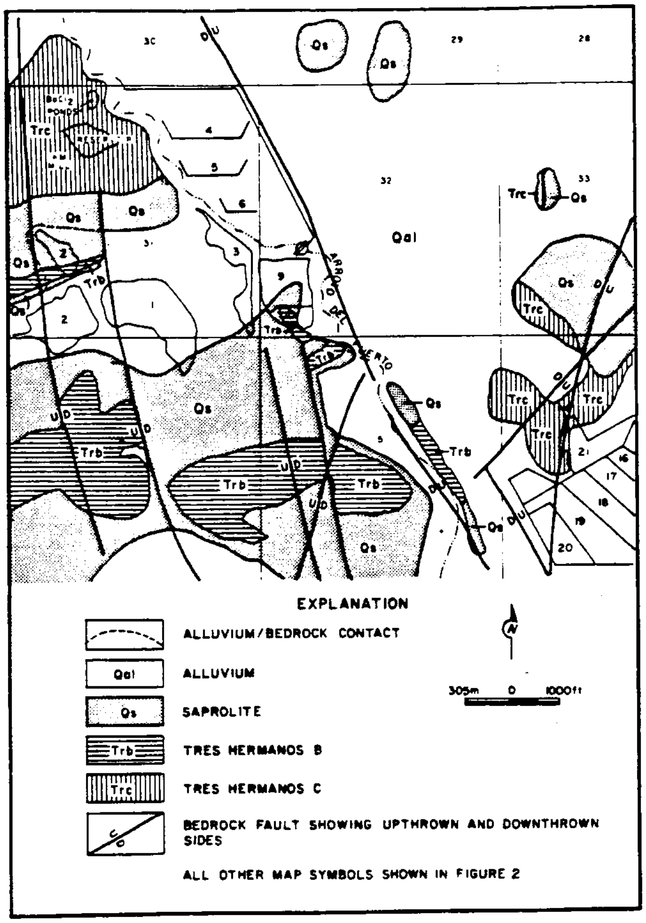

30
29
28
32
33
31
Qal
Qs
Trb
Trc
U
D
ARROYO DEL PUERTO
1
2
3
4
5
6
9
16
17
18
19
20
21
EXPLANATION
ALLUVIUM/BEDROCK CONTACT
Qal ALLUVIUM
Qs SAPROLITE
Trb TRES HERMANOS B
Trc TRES HERMANOS C
BEDROCK FAULT SHOWING UPTHROWN AND DOWNTHROWN SIDES
ALL OTHER MAP SYMBOLS SHOWN IN FIGURE 2
N
305m 0 1000ft

Figure 8. Map of Tres Hermanos and saprolite outcrops in Kerr-McGee millsite area. -- Adapted from Santos and Thaden (1966)

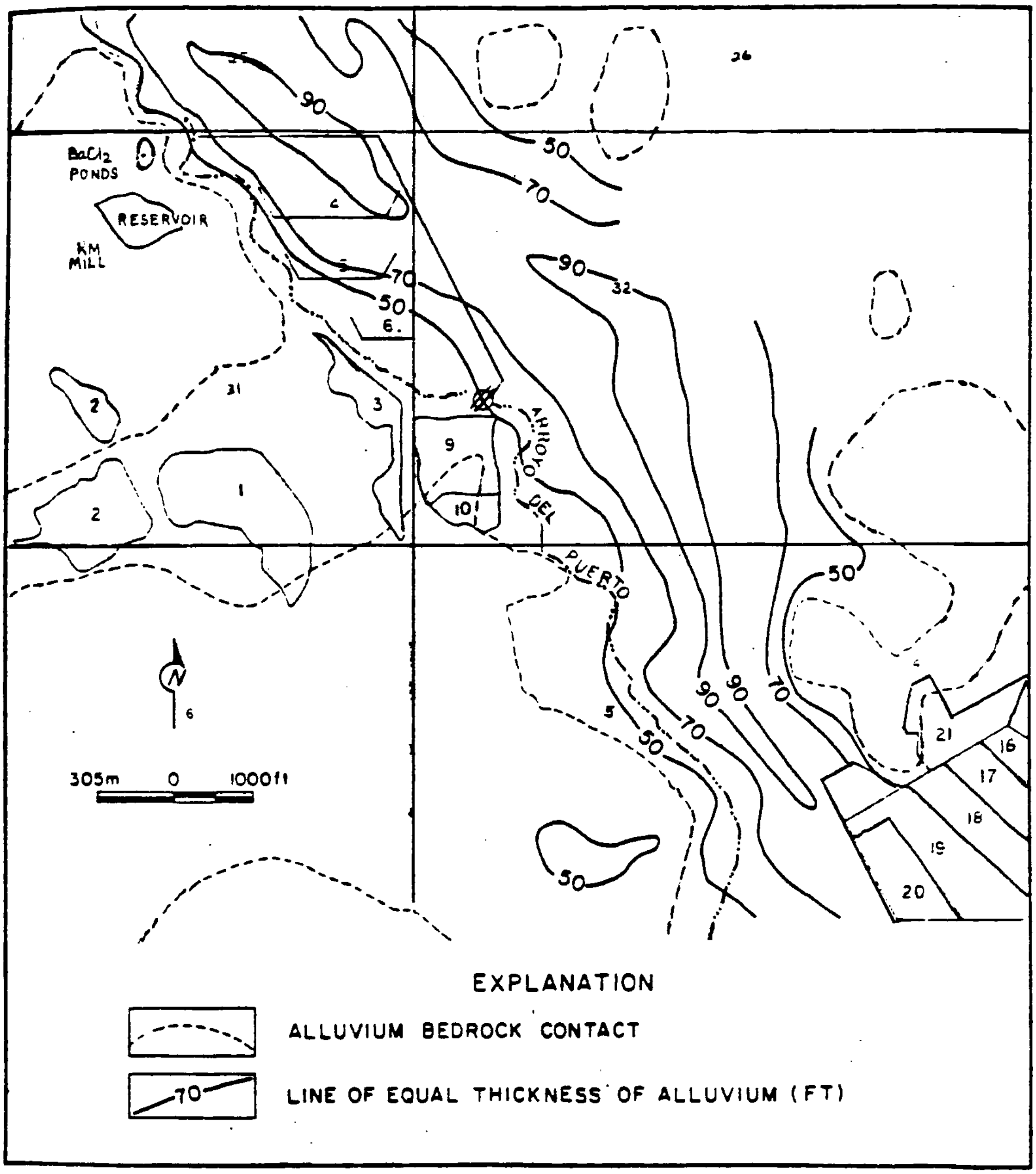

BaCl2 PONDS
RESERVOIR
KM MILL
90
50
70
90
32
50
6
31
2
3
9
10
1
2
ARROYO DEL PUERTO
50
90
90
70
70
50
5
50
26
21
16
17
18
19
20
N
305m 0 1000ft
EXPLANATION
ALLUVIUM BEDROCK CONTACT
70
LINE OF EQUAL THICKNESS OF ALLUVIUM (FT)

Figure 9. Isopach map of alluvium. -- From Ganus (1980, p. 19)

the alluvial material is fine-grained sand and clay with occasional basal gravel layers. Layering and stratification are commonly reported.

Little information exists describing the saturated condition of the alluvium prior to mining activities in the area. Kerr-McGee maintains that the alluvium was dry prior to the late 1950s before mines in the vicinity began discharging water into the ephemeral water courses below their facilities.

Kerr-McGee monitoring well #25 was developed in alluvial material 3 years after mining and milling began. At this site, a small saturated zone at the base of the alluvium was attributed to early mining activity. The well, in sec. 31, T. 14 N., R. 9 W., was destroyed in 1976 when Arroyo del Puerto was rerouted. Depth to water at that time was 75 ft (23.2 m), indicating that 10 ft (3 m) of alluvium was saturated.

Premining Hydrogeochemistry

Little chemical data exist for waters in the Ambrosia Lake area before mining began in the late 1950s, so that "background" concentrations of major dissolved species cannot be firmly established. Moreover, the three principal water-bearing units of this study, the Westwater Canyon, Dakota Sandstone, and alluvium-Tres Hermanos Sandstone, contain waters of varied chemical nature within a very small area. The chemical composition of these waters depends not so much on their depositional environment but rather on the diagenetic history of the deposits and the local conditions of ground-water recharge and movement (Brod, 1980). Stiff diagrams (Kelly and others, 1980) show

Westwater Canyon water is a Na–HCO_3–SO_4-type water and the Dakota Sandstone water is a Na-SO_4-type water, expressing the principal dissolved ionic species. Table 3 shows mine water discharge information (1957-1963) for early ranges in dissolved constituents from the Westwater Canyon and combined Westwater Canyon and Dakota waters. Sulfate concentrations in the Dakota are on an average twice those in the Westwater Canyon.

Samples from existing ranch and supply wells east and north of the millsite taken in the mid-1950s had sulfate concentrations less than 200 mg/L and chloride concentrations less than 25 mg/L and TDS

Table 3. Range in dissolved ion concentrations and pH in water from mine drainage, 1957-1963. -- Data from Cooper and John (1968).

	Westwater Canyon	Dakota + Westwater Canyon
Ca	6-53	6-140
Mg	<1-17	<1-56
Na	90-252	90-356
K	2.4-7.8	
HCO_3	209-300	209-340
SO_4	119-356	119-850
Cl	5-9	6-25
NO_3	<1-3.9	
pH	7.6-8.3	7.6-8.3

Well locations: T. 14 N., R. 9 W. and T. 14 N., R. 10 W.

between 400 and 600 mg/L. It is uncertain if these wells are open only in the Westwater Canyon or both the Dakota and Westwater Canyon formations (Ganus, 1980). A background sample from a well (#17-01) completed in the Dakota Sandstone showed SO_4^{2-} was 621 mg/L, Cl^-, 28 mg/L, TDS, 1,020 mg/L, and pH, 9.7 (Ganus, 1980). The alluvium near the millsite was considered dry prior to the late 1950s when uranium mining began (Ganus, 1980). Brod (1980) stated that ground water in most of the alluvium had a TDS from 500-1,000 mg/L before mine water discharge began. This contradictory statement may be referring to saturated alluvium along the San Mateo Creek valley and near its confluence with Arroyo del Puerto. However, parts of the alluvium in contact with the Tres Hermanos Sandstone Member probably contained some water prior to mining. East of the area near San Mateo and Mount Taylor the Tres Hermanos produces up to 900 gpm to mines in the area (Cooper and John, 1968). At the millsite, well #31-01 (fig. 10) completed in Tres Hermanos-B was artesian when drilled in 1977, not likely the result of mine discharge and pond infiltration. Brod (1980) described these waters as Na-SO_4-type with a high sulfate concentration near 2,500 mg/L and TDS of 2,500-9,000 mg/L from two observation wells near Kerr-McGee.

Mining and Milling Practices

Interpretation of the evolution of ground-water chemistry and flow regime in the study area is possible only within the context of the complex discharge history of the mine and mill water. Previously dry alluvium is now nearly saturated by effluents originating from at least

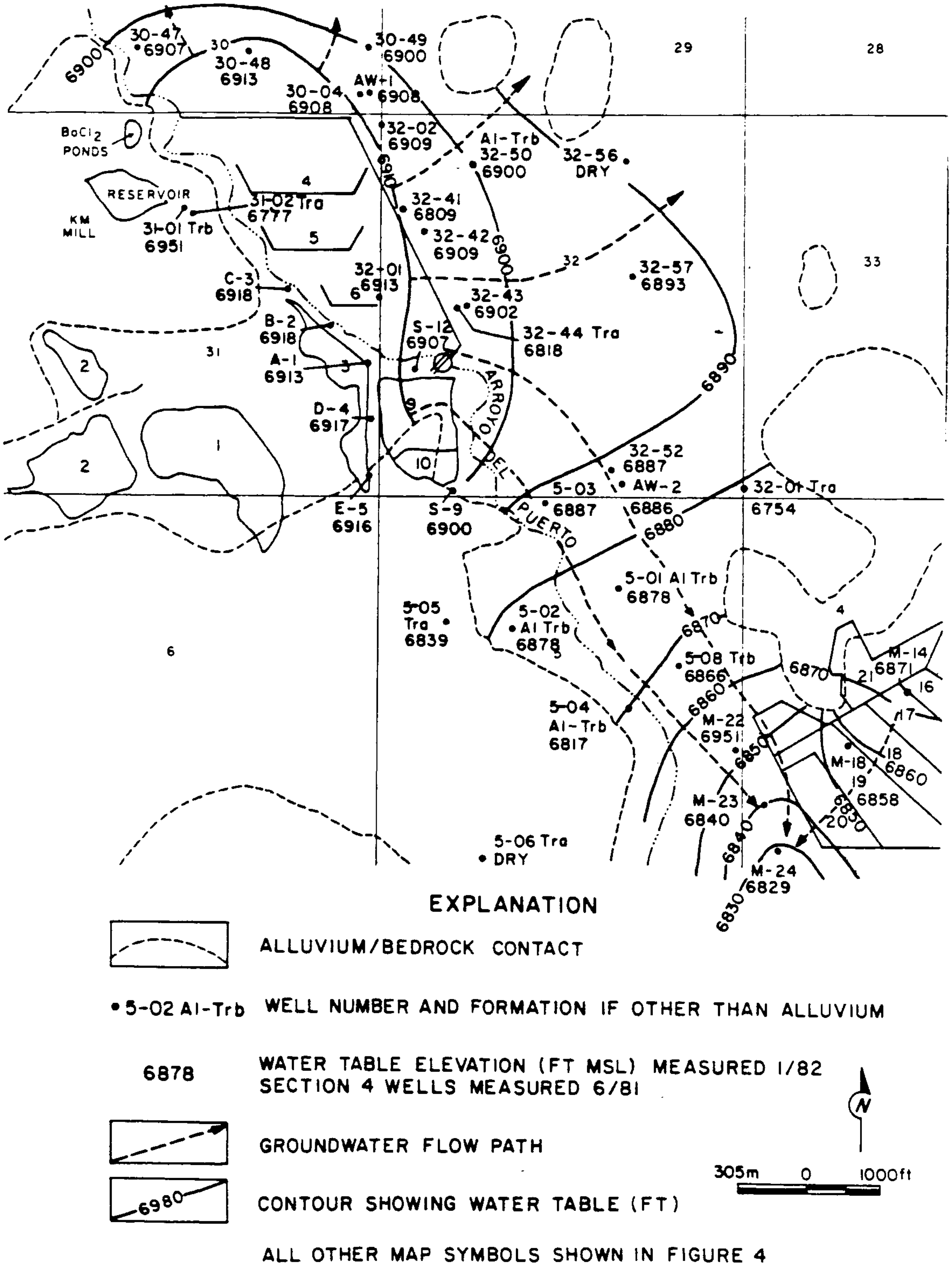

30-47
6907
30
30-48
6913
30-49
6900
30-04
6908
AW-1
6908
6900
BaCl2 PONDS
RESERVOIR
KM MILL
4
5
6
31-02 Tra
6777
31-01 Trb
6951
32-02
6909
Al-Trb
32-50
6900
32-56
DRY
32-41
6809
32-42
6909
6900
32-01
6913
32
32-57
6893
32-43
6902
32-44 Tra
6818
C-3
6918
B-2
6918
A-1
6913
D-4
6917
S-12
6907
31
2
2
1
3
9
10
ARROYO DEL PUERTO
6890
32-52
6887
AW-2
6886
6880
5-03
6887
32-01 Tra
6754
E-5
6916
S-9
6900
5-01 Al Trb
6878
5-05 Tra
6839
5-02
Al Trb
6878
6870
5-08 Trb
6866
6860
5-04
Al-Trb
6817
M-22
6951
6850
M-23
6840
6840
M-24
6829
6830
M-14
6871
6870
21
16
17
18
M-18
19
6858
6860
6850
20
5-06 Tra
DRY
29
28
33
4
6
EXPLANATION
ALLUVIUM/BEDROCK CONTACT
5-02 Al-Trb WELL NUMBER AND FORMATION IF OTHER THAN ALLUVIUM
6878 WATER TABLE ELEVATION (FT MSL) MEASURED 1/82
SECTION 4 WELLS MEASURED 6/81
GROUNDWATER FLOW PATH
6980 CONTOUR SHOWING WATER TABLE (FT)
ALL OTHER MAP SYMBOLS SHOWN IN FIGURE 4
N
305m 0 1000ft

Figure 10. Water-table map for alluvium, 1982

two sources, acidic mill pond leachate and relatively high quality mine dewatering discharge. Although several companies operate uranium mines and mills in the Ambrosia Lake area, this study focuses on only the Kerr-McGee industry effluents and their effect on the shallow alluvial system within 2 miles from the millsite.

Mine Water Discharge

Shaft construction and mine dewatering from the Westwater Canyon Member of the Morrison Formation began in 1957. At the bottom of the central shaft a sump collects ground water draining from beneath the orebodies and pumps it to an ion exchange plant where trace amounts of dissolved uranium are removed. Most of the water was directed into Arroyo del Puerto, causing perennial flow that reached San Mateo Creek and created a line source of recharge to the alluvium. Before National Pollution Discharge Elimination System (NPDES) laws were enacted in 1977, these mine waters received little chemical treatment beyond the economic removal of dissolved uranium. Now these waters are discharged to settling ponds where a flocculent and $BaCl_2$ are added to coprecipitate radium with $BaSO_4$ before river discharge. Ventilation shafts throughout the mining area, indicated on figure 5, allow water to drain from all permeable zones from ground surface to mine level. These mixed-formation waters were also pumped into Arroyo del Puerto.

Dissolved mineral content of mine water discharge was originally low but has steadily increased since mining began. In early 1960, mine water, primarily from the Westwater Canyon Sandstone Member, contained 200 mg/L SO_4^{2-}, 20 mg/L Cl^-, 600 mg/L TDS and had a pH of 7. In November 1982 mixed-formation mine waters discharged from the ion-exchange plant into the mill reservoir contained 1,188 mg/L SO_4^{2-}, 58 mg/L Cl^-, 2,056 mg/L TDS and had a pH of 8.1. This changing chemistry probably reflects mining practices such as water recirculation to leach additional uranium from mined areas and backfill operations that emplace mill tailings within mined-out areas to prevent roof collapse.

Additional recharge through the alluvium came from an unlined ditch that traversed from section 36 to section 31. The ditch, in use from the late 1950s to mid-1960s, delivered dewatering discharge from sections 35 and 36 mines to the mill. Total discharge from both mines was 2,500 gpm. Presently the section 35 mine pumps a variable, sometimes large, amount of water from the Dakota Sandstone. Dakota ground water in this area had a sulfate concentration of 1,500-2,000 mg/L.

When milling operations began in October 1958 most mine dewatering discharge was diverted to a mill reservoir to be used in the milling process. This reservoir was constructed on locally clay-poor materials, and seepage loss has been large. A Kerr-McGee water budget based on 1979 usage data estimates 270 gpm seepage loss from this reservoir (Ganus, 1980). Excess mine water, beyond milling process requirements, has always been pumped to Arroyo del Puerto. In 1976 the course of Arroyo del Puerto was realigned near the millsite to divert potential flood flows around ponds and tailings (fig. 5).

Milling Process

The 7,000 ton per day Kerr-McGee mill is the largest uranium mill in the United States (Mining Engineering, 1974). The milling process removes and concentrates the uranium from the crushed ore, using approximately 1,380 gpm (1979 Kerr-McGee water budget; Ganus, 1980) of water from the mill reservoir. The section 31 mill operations include the mill reservoir, tailings impoundment (pond #1) decant pond (pond #3), and evaporation ponds (ponds #4-#20). Evaporation ponds #11 through #20 located in section 4 are lined and are reported not to leak. Table 4 lists the physical characteristics of ponds #1 through #10 and data of their construction or operation at the millsite. The total seepage from unlined ponds #1-#8 is roughly estimated from 1979 figures (Ganus, 1980) to be 203 gpm.

A schematic abstracted from Mining Engineering (1974) is shown in figure 11. Mine waters from the mill reservoir are mixed with large quantities of sulfuric acid and sodium chlorate to leach oxidized uranium from the crushed ore. The acid water in the mill circuit (pH = 0.5) also dissolves gangue minerals such as vanadium, selenium, molybdenum, and other metals. In stage 3, solid tailings are separated into sands and slimes based on particle size from the uranium-rich solution. The "pregnant" solution of dissolved uranium enters stage 4, solvent extraction, in which uranium is concentrated and removed by an organic solvent and ion exchanger. Chloride, as NaCl, is added in the solvent extraction cycle to strip uranium ions from the organic solvent by anion replacement.

Table 4. Physical characteristics of Kerr-McGee ponds #1 through #10, 1979. -- Data from Ganus (1980)

Pond #	Area (acres)[a]	Volume (acre-ft)[a]	Date of Construction	Remarks
1	62	372	1958	unlined
2	46	299	1958	unlined; in contact with Tres Hermanos (outcrop)
3	27	53	1958	unlined
4	13	26	1958	unlined
5	11	16	1958	unlined
6	8	16	1958	unlined
7	12	13	1961	unlined; in contact with Tres Hermanos (outcrop)
8	24	24	1961	unlined; in contact with Dakota (outcrop)
9	24	73	1976	plastic lined
10	7	17	1976	plastic lined; needs remedial work
TOTALS (approx.)	234	909		

a. Maximum reported in 1979.

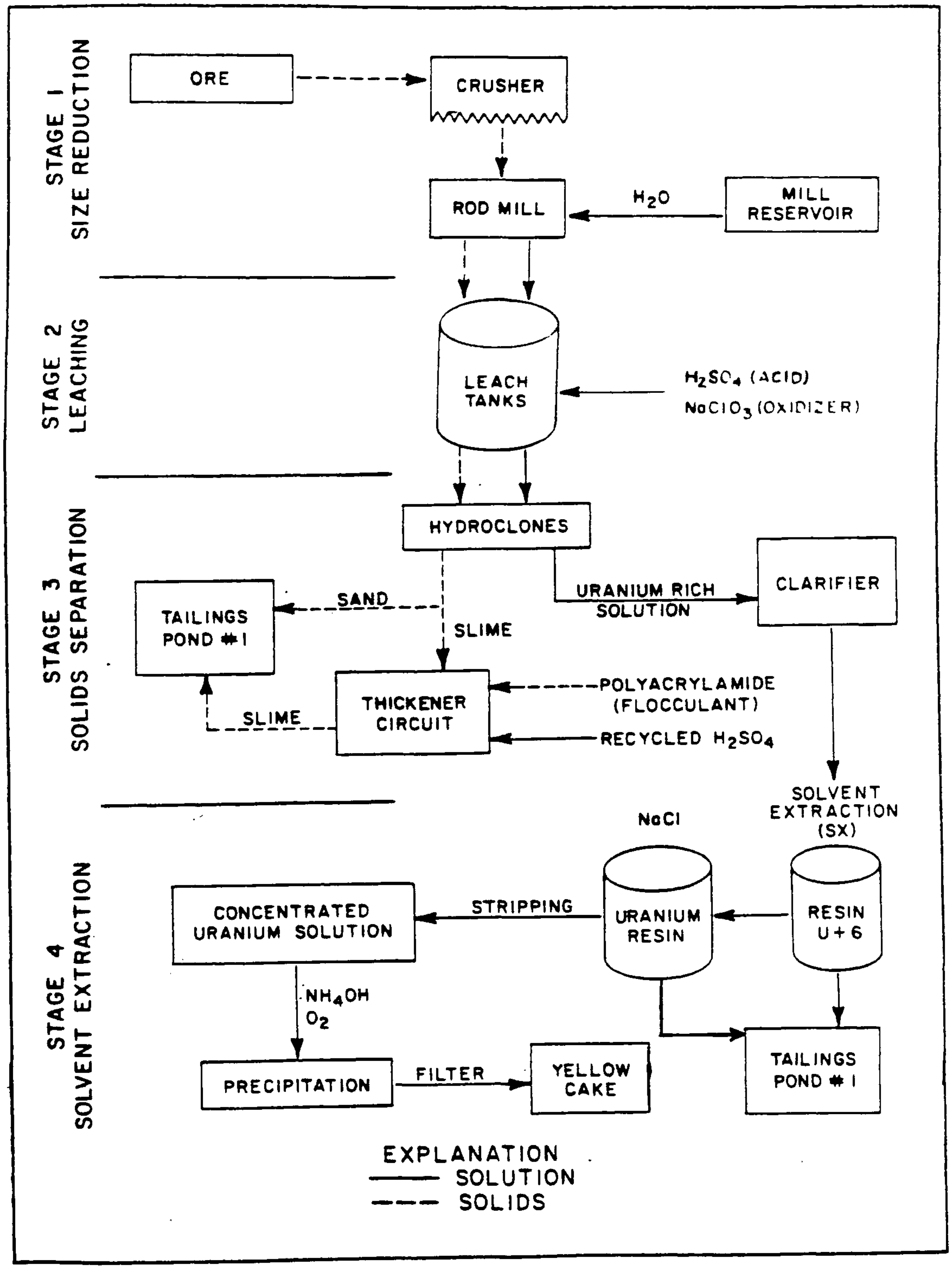

STAGE 1
SIZE REDUCTION
ORE
CRUSHER
ROD MILL
H_2O
MILL RESERVOIR
STAGE 2
LEACHING
LEACH TANKS
H_2SO_4 (ACID)
$NaClO_3$ (OXIDIZER)
STAGE 3
SOLIDS SEPARATION
HYDROCLONES
URANIUM RICH SOLUTION
CLARIFIER
SAND
SLIME
TAILINGS POND #1
THICKENER CIRCUIT
POLYACRYLAMIDE (FLOCCULANT)
RECYCLED H_2SO_4
SLIME
STAGE 4
SOLVENT EXTRACTION
SOLVENT EXTRACTION (SX)
NaCl
CONCENTRATED URANIUM SOLUTION
STRIPPING
URANIUM RESIN
RESIN U+6
NH_4OH
O_2
PRECIPITATION
FILTER
YELLOW CAKE
TAILINGS POND # 1
EXPLANATION
——— SOLUTION
– – – SOLIDS

Figure 11. Schematic of Kerr-McGee uranium leach circuit. -- Adapted from Mining Engineering (1974, v. 26, no. 8, p. 28-30).

The tailings are slurried with the "barren" uraniumm-stripped waste water and pumped to the tailings pond (pond #1). In 1960, the tailings-pond solution contained 26,000 mg/ sulfate, 2,000 mg/L chloride, 40,000 m/L TDS and had a pH between 1 and 2. Excess fluid from pond #1 is decanted to pond #3. Pond #3 also receives water with lower total dissolved solids derived from the diversion of Arroyo del Puerto, which collects seepage from the ponds. Concentrations of all dissolved species are significantly less in pond #3 than in pond #1. Periodically, excess fluid from pond #3 is pumped to the various evaporation ponds.

Present Hydrologic Conditions

There are two chemically distinct types of uranium industry effluents recharging the alluvial system: (1) recharge by seepage from mill ponds #1 through #10 and (2) recharge by infiltration of mine waters along conveyance ditches and Arroyo del Puerto and from seepage beneath the mill reservoir.

Flow Characteristics

The water-level data shown on figure 10, which was constructed from January 1982 data provided by Kerr-McGee, indicates that, at least east of Arroyo del Puerto, the Tres Hermanos-B is in hydraulic contact with alluvium. Water in the Tres Hermanos-A is confined or semi-confined by interlayered Mancos Shale. Water levels reported by Brod (1980) and Ganus (1980) are similar to those measured in 1982.

Figure 12, taken from Ganus (1980), is a conceptual model of present-day flow conditions in the alluvium. The new creek represents

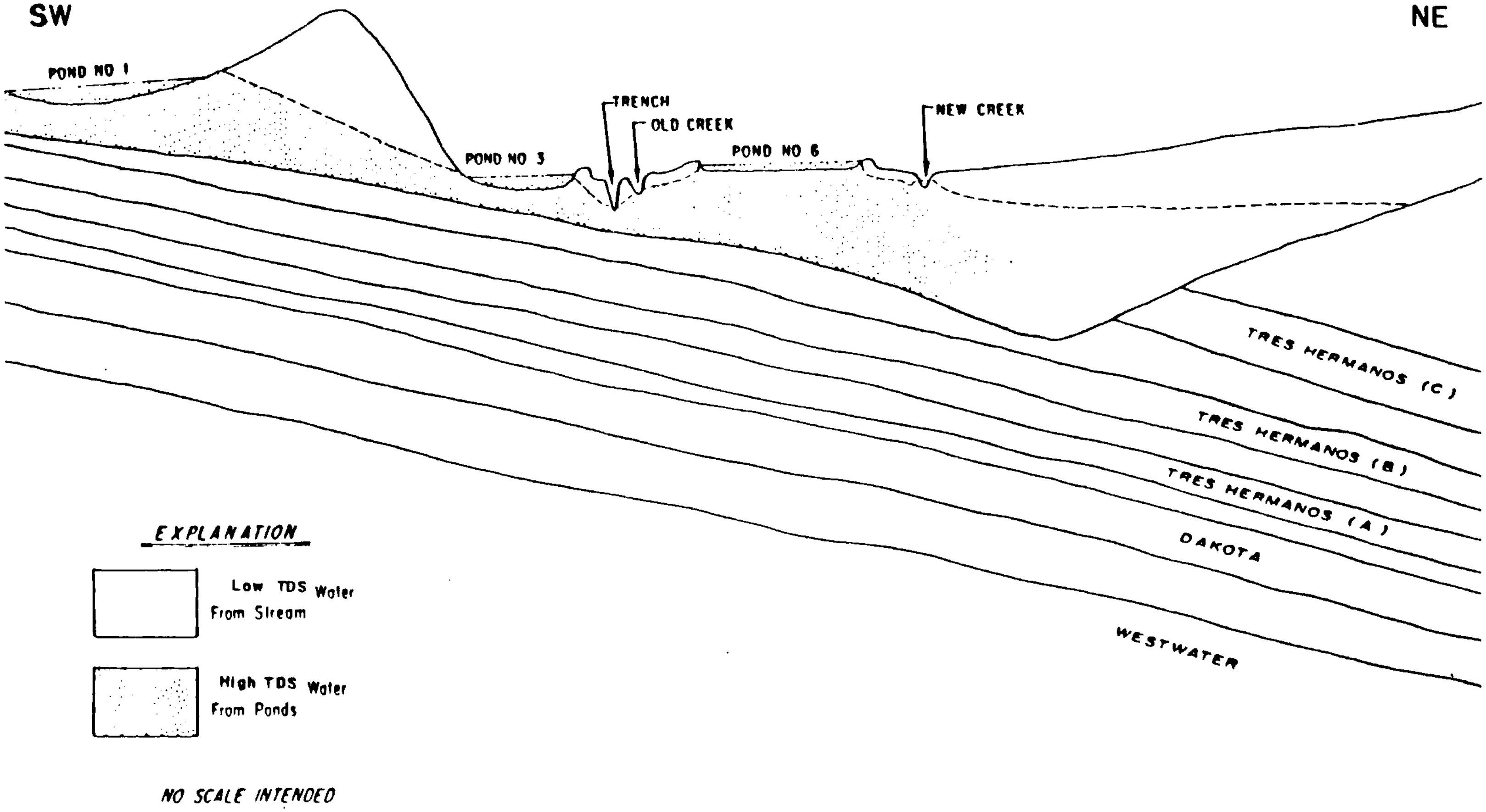

SW
NE
POND NO 1
POND NO 3
TRENCH
OLD CREEK
POND NO 6
NEW CREEK
TRES HERMANOS (C)
TRES HERMANOS (B)
TRES HERMANOS (A)
DAKOTA
WESTWATER
EXPLANATION
Low TDS Water From Stream
High TDS Water From Ponds
NO SCALE INTENDED

Figure 12. Southwest-northeast cross section showing present conditions in alluvium. -- After Ganus (1980)

the diversion of Arroyo del Puerto and shows that the water table is at the creek bottom along this reach. The trench was excavated in 1959 to intercept pond seepage, which is then returned to pond #3. A large ground-water mound formed in the alluvium by seepage from ponds and Arroyo del Puerto is moving fluid to the north, east, and southeast. Water-table contours (fig. 10), indicate that fluid movement to the east is presently slower than to the north or southeast. The water-table gradient east is gentle because the Arroyo del Puerto bottom acts as a limiting factor to build-up in mound height.

Ground-water flow velocity in the saturated zone is a function of water-table gradient, hydraulic conductivity, and effective porosity. The average hydraulic conductivity of the alluvium is 10 gpd/ft^2 (1.3 ft/day), based on aquifer tests at wells in section 32. From the water-level contours shown on figure 11 and an effective porosity assumed to be 20 percent, approximate flow velocities of 35 ft/yr to the north, 12 ft/yr to the east, and 22 ft/yr to the southeast have been calculated. Volumetric flow rates determined by using these velocities and a saturated thickness of alluvium are 25 to 30 gpm flow to the north, 15-20 ppm flow to the east, and about 10 gpm flow to the south.

The similarity between 1980 and 1982 water levels shows that the alluvial aquifer is now approaching steady-state flow. Near the millsite the alluvium is nearly saturated to the surface. A National Dam Safety Program inspection report (New Mexico State Engineer, 1979) reports seeps coming from the alluvium below the base of the tailings dam well above adjacent ponds and a boil on a flat area between pond #1 and the nearby evaporation ponds. No potentiometric data exist for pond fluid migration, so the ground-water flow system beneath the ponds is poorly understood.

Water-quality Conditions

The figure 12 cross section from the southwest of pond #1 to the northeast across the alluvial valley depicts high TDS, poor-quality seepage from the ponds mixing with infiltrating higher quality mine discharge water along the Arroyo del Puerto, which moves toward the deepest part of the alluvium. The first two monitoring wells completed in alluvium at the site showed increasing chloride concentration with water-level rise, indicating a dilution or dispersion front expected from mixing tailings solution with high-quality water from Arroyo del Puerto. Water samples (November 1981) from the alluvium and alluvium– Tres Hermanos wells show large differences in concentrations of major ions even within close proximity. These large quality differences can be attributed to (1) disparate quality waters recharging the alluvium, (2) a complex recharge history, and (3) geochemical interactions between recharging waters and underlying formation materials.

The quality of mine-water recharge depends on the relative quantities of different formation waters being discharged from the various operating mines. With respect to water chemistry, the ponds may be grouped into two classes: ponds #1 and #2 in contact with the solid tailings, which have high concentrations of dissolved species, and (2) ponds #3 through #8 in contact with natural earth surface materials, which contain reduced amounts of dissolved ions. Two different sets of conditions exist for pond seepage into the alluvial system.

Interaction of Mill Effluent with Tailings and Alluvium

Alluvial pond recharge via seepage requires that liquid contained in the ponds travel through the natural earth foundation and, in the case of pond #1, through the sand and slime tailing wastes. In either case, the liquid effluent encounters a very different sequence of chemical conditions, each requiring that a new chemical equilibrium be established. The resultant recharge entering the alluvial system will be of a significantly different chemical composition from the original pond effluent.

Physical Characteristics of the Tailings Pond. Pond #1, south of the mill, is the main tailings pond impoundment (fig. 13). Pond #2 was previously used for tailings disposal, but the following descriptions concern only the main impoundment. The tailings pond began as a starter dam, 10-ft (3.0 m) high, on local clayey material. Dam construction is a continuing process by which sands deposited from the tailings slurry are pushed up as a berm along the perimeter. The pond now rests about 100 ft (30.5 m) above the streambed elevation, and it is raised in proportion to the total volume of solids added as tailings. Surveyed from the crest of the berm, the impoundment resembles a wide beach with progressively more saturated finer materials approaching the fringe of the solution area.

The underlying alluvium is generally less than 7 ft (2.1 m) thick and rests on sandstone and shale units of the Mancos Formation. The U.S. Geological Survey Map GQ-515 (Santos and Thaden, 1966) shows north-trending normal faults crossing beneath the middle and upper

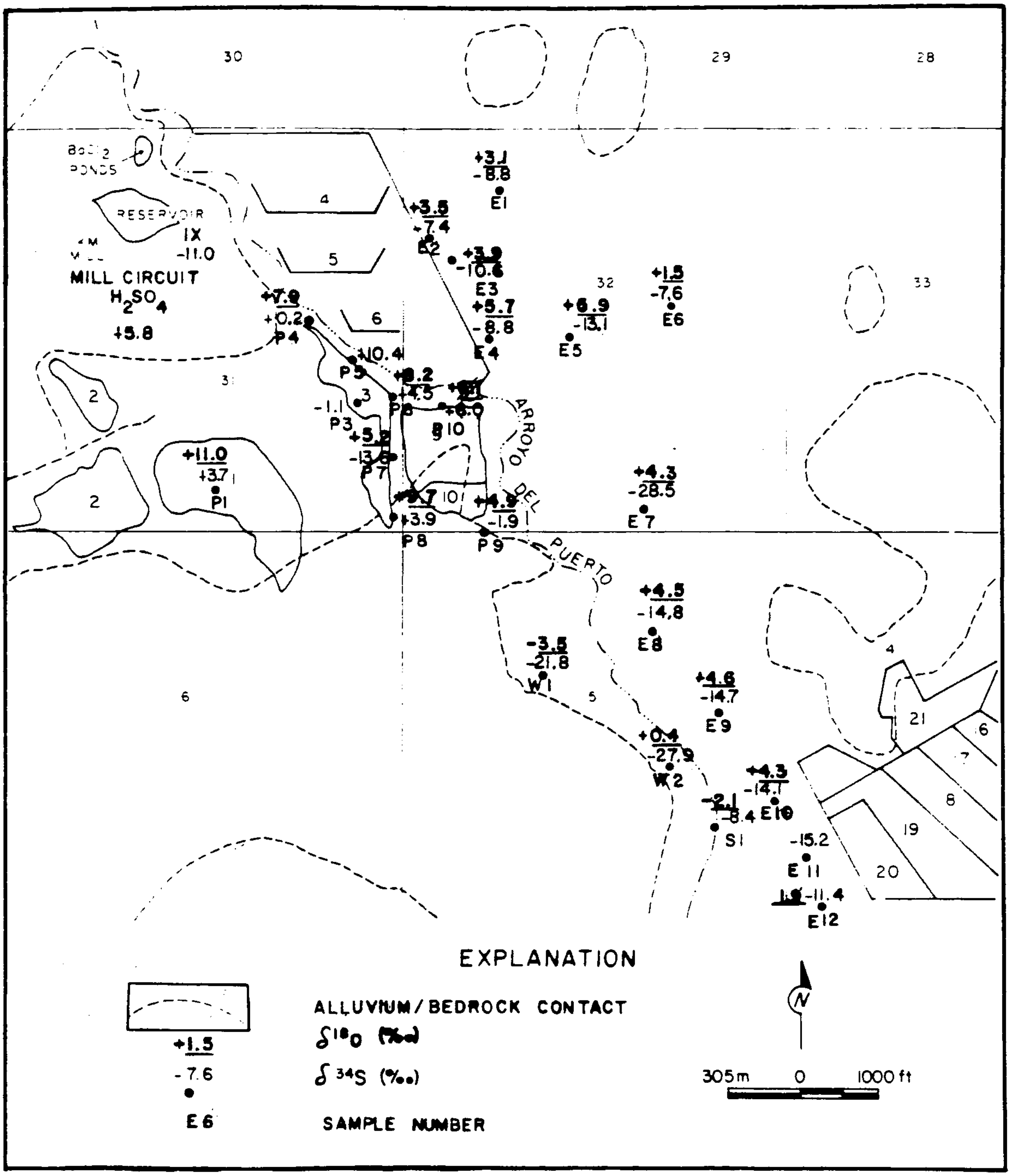

30
29
28
32
33
31
BaCl2 PONDS
RESERVOIR
IX
-11.0
MILL CIRCUIT
H_2SO_4
+5.8
4
5
6
2
2
+3.1
-8.8
E1
+3.5
-7.4
E2
+3.9
-10.6
E3
+5.7
-8.8
E4
+6.9
-13.1
E5
+1.5
-7.6
E6
+4.3
-28.5
E7
+4.5
-14.8
E8
+4.6
-14.7
E9
+4.3
-14.1
E10
-15.2
E11
-11.4
E12
+7.9
+0.2
P4
+10.4
P5
3
-1.1
P3
+5.2
-13.6
P7
+11.0
+3.7
P1
+8.2
+4.5
P6
+6.0
P10
10
+3.9
P8
+4.9
-1.9
P9
ARROYO DEL PUERTO
-3.5
-21.8
W1
+0.4
-27.9
W2
-2.1
-8.4
S1
21
6
7
8
19
20
EXPLANATION
ALLUVIUM/BEDROCK CONTACT
+1.5
-7.6
E6
δ18O (‰)
δ34S (‰)
SAMPLE NUMBER
N
305m
0
1000 ft

Figure 13. Sampling sites and sulfate isotope values

portions of tailings ponds #1 and #2 (New Mexico State Engineer's Office, 1979).

The tailings impoundment has grown proportionately with the amount of ore processed at the mill. Both the depth and relative size and position of the fluid area have shifted over a 23-year history. In this time span, ponds #3 through #8 have also been employed, receiving different amounts of mill-pond effluents in accordance with the mill operating history. These shifting conditions make it impossible to apply a predictive analytical model to describe the pond seepage history even if a piezometric monitoring program were to be installed at this time (Morin and others, 1982). A conservative, long-term, stable pond constituent provides a better way to characterize pond seepage migration.

Attenuation of Contaminants. Dissolved constituents in mill-pond effluent are removed by sorption, precipitation, and coprecipitation reactions. Four chemical parameters influencing the course of these reactions are pH, redox potential (Eh), ionic strength, and the nature of the solution or types of dissolved species. In the use of sulfate isotopes as seepage tracers, it is important to determine how much sulfate is attenuated by adsorption onto tailings or earth materials or by precipitation within the system.

The ability of a chemical constituent to move through a porous medium can be estimated by measurement of its distribution coefficient (Kd), which expresses the mass ratio of a solute between solid and liquid ($Kd = C_{solid}/C_{solution}$) at a given point in a ground-water flow system. Measured distribution coefficients incorporate the effects of reversible and irreversible sorption, precipitation, and/or coprecipitation reactions.

The use of distribution coefficients is questionable in subsurface contaminant migration situations (Reardon, 1981). Groundwater chemistry in a seepage scenario is in a state of dynamic chemical evolution whereby water chemistry varies in space and time until sorbed-site ion population and precipitation reactions reach a steady state at each point in the flow system. For this reason, laboratory Kd values for sulfate were not measured using alluvium and tailings solids.

Anions such as chloride and nitrate, and to a lesser extent sulfate, normally pass through soils without significant sorption. However, under acidic conditions clay particle edges, metal oxides, and humic materials protonate, develop discrete positive surface charges, and become anion absorbers. This condition would most likely occur in the slimes or clayey layer that settles out between the coarser tailings and the tailings pond foundation material.

Alkaline earth materials in the Ambrosia Lake area present a significant barrier to sulfate migration by their ability to neutralize penetrating leachate and precipitate sulfate. Acid is neutralized primarily by the following reaction with carbonates in which sulfate is precipitated mainly as gypsum:

$$\underset{\text{calcite}}{CaCO_3} + SO_4^{2-} + 2H^+ \rightleftarrows \underset{\text{gypsum}}{CaSO_4 \cdot 2H_2O\downarrow} + CO_2$$

Markos and Bush (1981) observed precipitation bands of iron, manganese, and gypsum in an interface zone between tailings and the subsoil in cores taken from an abandoned tailings site. Precipitated gypsum often forms a coating around the calcite, preventing further dissolution. Kerr-McGee (Ganus, 1980) estimates that $CaCO_3$ makes up 2 percent of the alluvial foundation material. This is sufficient calcite such that all H_2SO_4 could theoretically react to produce $CaSO_4$ (Rahn and Mabes, 1978). However, sulfate much exceeds the hydrogen ion (H^+) concentration, because much acidity is consumed in stages of the milling process. As low pH water continuously enters the alluvial sands, all the calcium carbonate in a unit area is eventually dissolved, then the low-pH water advances to the next area of alluvial material.

Sulfate is present in extremely high concentrations in uranium tailings ponds (37,400 mg/L in pond #1 on November 9, 1981). Some sulfate removal by sorption and precipitation in the neutralization zone occurs, but residual leachate concentrations are still very high, ranging from 3,000 to 8,000 mg/L (table 5) in wells adjacent to mill ponds. Neither adsorption nor precipitation should significantly alter isotopic composition in remaining dissolved sulfate, so the identity of each sulfate source is maintained despite the reduction in absolute concentration.

Table 5. Chemical and isotopic characteristics of water samples from the Kerr-McGee millsite

		Field Measurements					Major Ions (mg/L)[a]								SO_4		H_2O
Sample Number	Sample Location or Well #	T (°C)	pH	Specific Conductivity (µmhos)	H_2S (mg/L)	Water Elevation (ft, MSL)	Na^+	Ca^{+2}	Mg^{+2}	K^+	HCO_3^-	SO_4^-	Cl^-	TDS	$\delta^{34}S^b$ (°/oo)	$\delta^{18}O^c$ (°/oo)	$\delta^{18}O^c$ (°/oo)
S2	IX discharge	16	8.1	2,050	-	-	292.1	226.5	70.0	9.75	194.7	1,188	58.3	2,056	-11.0	-	-11.4
P1	Pond #1	14.5	1.4	36,000	-	-	1,327.0	755.7	1,194.8	109.2	<1	37,483	2,774.4	44.484	+ 3.7	+11.0	- 8.2
P3	Pond #3	-	-	-	-	-	800.4	410.9	509.2	24.6	<1	6,454	989.8	10,844	- 1.1	-	- 9.5
S1	Cattails P-12	-	-	-	N	-	226.8	206.0	45.8	16.4	204.1	1,034	249.1	1,956	- 8.4	- 2.1	-10.5
P1A[d]	mill discharge	-	1.4	>50,000	N	-	1,316.0	895.0	1,991.2	112.5	<1	38,327	2,608.1	41,960	-	+ 9.8	-10.0
	Arroyo del Puerto (P-10)	-	-	-	N	-	278.3	206.4	78.7	16.4	196.1	1,008	237.1	1,948	-	-	-
P6	A1	17.5	6.38	-	N	6,911.66	1,750.0	384.0	1,264.3	21.1	<1	7,913	3,969.3	16,404	+ 4.5	+ 8.2	- 5.7
P5	B2	17.4	5.5	-	N	6,913.90	1,021.0	346.7	439.1	3.51	<1	3,669	4,038.2	10,564	+10.4	-	- 8.4
P4	C3	18.4	5.07	-	N	6,913.25	1,115.0	485.2	947.3	9.75	<1	4,527	3,479.9	11,556	+ 0.2	+ 7.9	- 6.6
P7	D4	17.6	5.5	-	N	6,912.32	197.8	1,056.0	343.4	10.14	<1	867	2,836.8	6,200	-13.6	+ 5.2	- 5.8
P8	E5	-	7.8	-	N	6,914.24	1,260	159.2	881.5	22.6	1,269.9	3,053	2,180.8	8,332	+ 3.9	+ 9.7	- 6.5
P9	S9	14.0	8.4	10,000	N	6,899.87	968.3	49.6	1,661	13.3	561.1	4,827	2,499.5	11,360	- 1.9	+ 4.9	- 5.6
P10	S12	17.6	6.73	-	N	6,906.52	2,203	303.1	1,388.7	1,755	2,137.6	5,594	3,078.7	14,312	+ 0.0	+ 0.1	- 5.0
E-8	5-01	12.8	7.5	2,050	N	6,875.76	269.1	212.8	149	1.56	49.5	1,445	170.4	2,396	-14.8	+ 4.5	-11.8
W1	5-02	13.9	8.5	4,330	N	6,878.08	379.5	619.5	273.5	0.78	88.4	1,908	1,129.9	4,882	-21.8	- 3.5	- 7.8
E13	5-03	12.9	7.4	3,170	N	6,886.41	308.2	384.5	209.3	1.56	316.2	1,887	413.1	3,672	-	-	-
W2	5-04	13.8	8.7	3,130	N	6,869.51	103.7	343.9	398.7	6.63	12.1	2,709	123.8	3,698	-27.9	+ 0.4	-10.5
E9	5-08	11.7	9.2	2,070	0.3	6,865.82	223.1	148.6	178.9	7.02	47.1	1,373	139.8	2,244	-14.7	+ 4.6	- 9.5
E2	32-41	12.0	8.1	5,600	N	6,908.79	540.7	136.6	743.5	10.92	60.41	2,907	1,137.1	6,064	- 7.4	+ 3.5	- 8.2
E3	32-42	13.8	7.4	10,000	N	6,908.73	1,888	539.0	861.2	2.73	717.2	5,850	1,534.7	11,868	-10.6	+ 3.9	- 7.6
E4	32-50	14.1	7.1	5,700	N	6,904.28	671.1	484.0	486.5	9.75	590.6	3,563	123.7	6,468	- 8.8	+ 5.7	-
E1	32-50	14.2	7.2	7,400	N	6,899.76	1,102	570.4	453.5	3.90	537.5	3,034	1,645.4	7,536	- 8.8	+ 3.1	- 7.4
E5	32-51	13.7	8.6	4,380	N	6,897.33	680.8	452.8	341.6	1.66	258.2	3,440	182.4	5,424	-13.1	+ 5.9	- 9.7
E7	32-52	15.1	9.1	2,750	N	-	317.4	323.0	177.6	3.90	19.6	2,087	88.9	3,120	-28.5	+ 4.3	- 8.8
E6	32-57	13.7	7.6	5,500	N	6,893.37	1,402	390.4	296.1	8.19	458.0	4,334	207.4	7,148	- 7.6	+ 1.5	- 8.3
E10	M-22	12.9	7.5	3,170	N	6,851.50	393.3	481.6	195.0	0.78	227.3	2,485	83.9	4,064	-14.1	+ 4.3	-10.3
E11	M-23	12.3	7.2	4,890	N	6,840.41	918.9	549.0	180.3	4.49	225.0	2,614	130.5	5,968	-15.2	-	-
E12	M-24	13.2	7.2	3,200	N	6,830.11	315.1	577.2	163.5	2.34	300.3	2,005	132.1	3,928	-11.4	+ 1.9	- 8.5

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a. New Mexico State Laboratory, Albuquerque. b. University of Arizona Laboratory of Isotope Geochemistry, Tucson.
c. U.S. Geological Survey, Isotope Branch, Denver. d. To pond #1.

CHAPTER 4

SAMPLE COLLECTION AND ANALYTICAL METHODS

Sample Collection

Samples were collected November 9 and 10, 1981 from monitoring wells, mill ponds, and Arroyo del Puerto. Wells were sampled by bailer, and pond and river samples were obtained as "grab" samples. At each sampling point in figure 13, two 1-liter polyethylene containers were filled with water for sulfate isotope analysis. Apporixmately 10 ml of formaldehyde were added to each container to prevent possible bacterial sulfate reduction. A Hach Kit© (Loveland, Colorado) test for hydrogen sulfide was performed on each well sample to detect possible bactierial sulfate reduction under reducing conditions within the formation waters. Only one well, E-9, showed detectible sulfide. Other field measurements at each sampling location included temperature, pH, conductivity, and depth to water (table 5). Water samples were collected by representatives of the New Mexico Environmental Improvement Division (EID) for major ion, trace element metal, and stable oxygen and hydrogen isotopic analysis. Water samples for deuterium and oxygen-18 analyses were collected in 100-ml glass bottles and caps were sealed with paraffin. This study includes the EID data for major ion and oxygen-18 analyses for water samples. Samples were filtered through a Millipore© (Bedford, Massachusetts) 0.45-micron cellulose acetate membrane filter at the time of collection.

Analytical Methods

Sulfate Isotopes

A detailed description of the analytical procedures for both sulfur-34 and oxygen-18 analyses is provided in the appendix. Sulfate was precipitated from filtered samples as $BaSO_4$. The $BaSO_4$ was converted to sulfur dioxide (SO_2) gas within a vacuum line and analyzed for sulfur-34 at the University of Arizona Laboratory of Isotope Geochemistry. Barium sulfate was converted to CO_2 in Robert Rye's laboratory at the U.S. Geological Survey Isotope Branch in Denver, Colorado, and the CO_2 was analyzed for sulfate oxygen-18 on the Micromass-602C mass spectrometer in the Laboratory of Isotope Geochemistry with the help of Austin Long. All sample preparation and analyses were carried out by the author.

Water Isotopes

Analyses for oxygen-18 and deuterium on water samples were submitted by the New Mexico EID to the University of Arizona Laboratory of Isotope Geochemistry. Oxygen-18 isotope measurements are included in this report with permission by Bruce Gallaher, New Mexico EID. Oxygen-18 measurements were made on CO_2 gas collected by the CO_2 equilibrium method described by Epstein and Mayeda (1953).

Chemical Data

Major ion and trace-metal analyses were performed on the New Mexico EID samples by the New Mexico State Laboratory, Albuquerque, New Mexico. Permission to use the data was granted by EID. All analyses were performed according to standard procedures.

CHAPTER 5

INTERPRETATION AND DISCUSSION OF RESULTS

Table 5 shows analytical results. Column 2 of the table identifies samples by location or Kerr-McGee monitoring well number. Sample designations in column 1 indicate the location of the sample relative to ponds and river. Sample locations and designations and sulfate isotopic composition are shown in figure 13. Chemical and isotopic correlations were plotted on figures 14-19.

The data collected for this study on November 9 and 10, 1981 give a snapshot picture of chemical and isotopic values at coordinate points around the millsite. Chemical concentrations of samples dissolved in ground waters depend on geochemical conditions along the pathway of the species, the geochemical behavior of the species, and the pathway followed by the species. For these reasons, data of water chemistry show considerable variation between neighboring sampling sites and between sampling visits. Isotopic values for species dissolved in ground waters are not expected to show as great a temporal or spatial variation as concentrations of dissolved constituents. Consequently sulfate isotopic composition correlations ^{18}O and ^{34}S (figs. 18–19) show more distinctive groupings than do the isotopic-chemical correlations (figs. 14-17). A quantitative assessment of pond leachate into the alluvium can be made based on dissolved sulfate isotopes and water oxygen isotopes.

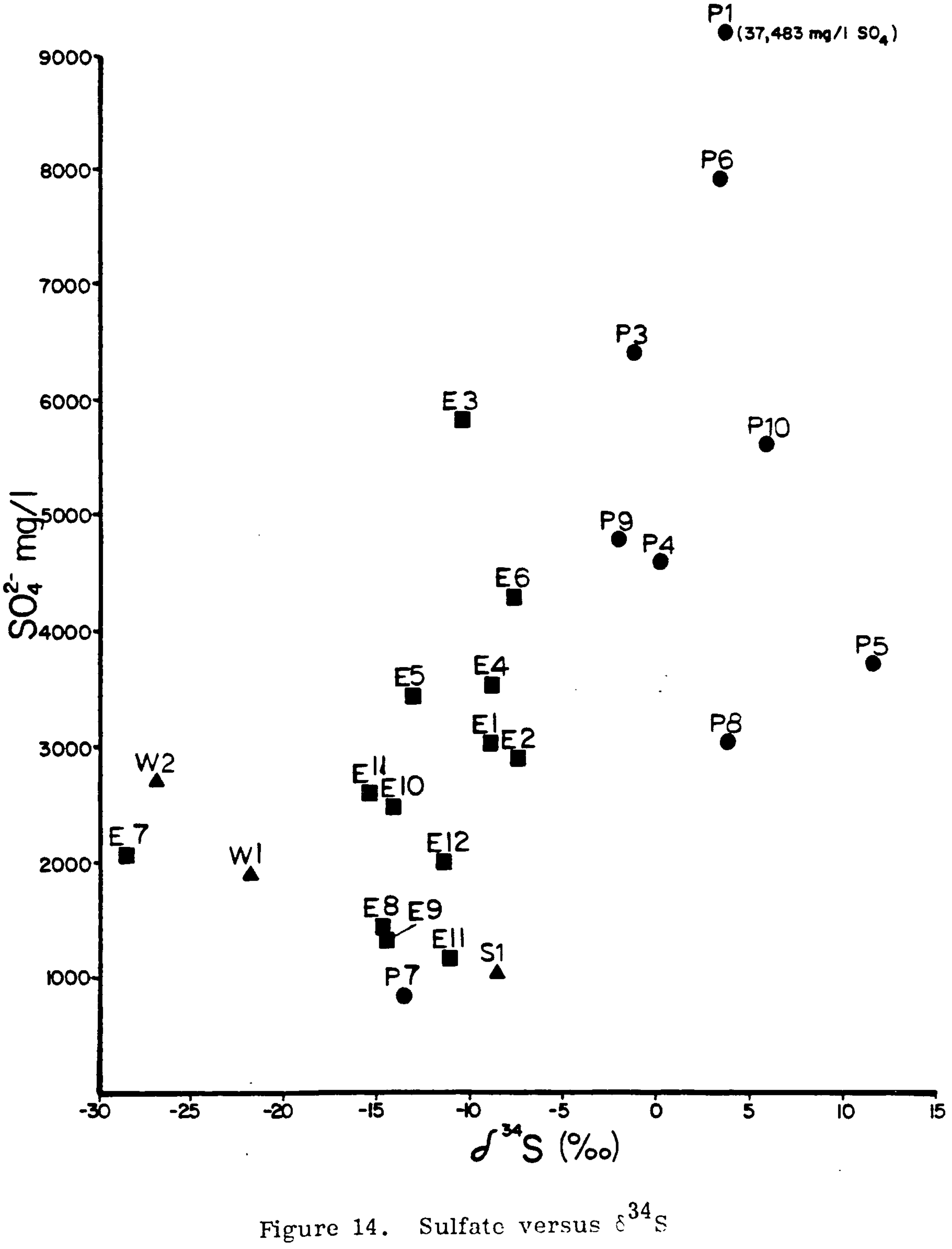


Figure 14. Sulfate versus $\delta^{34}S$

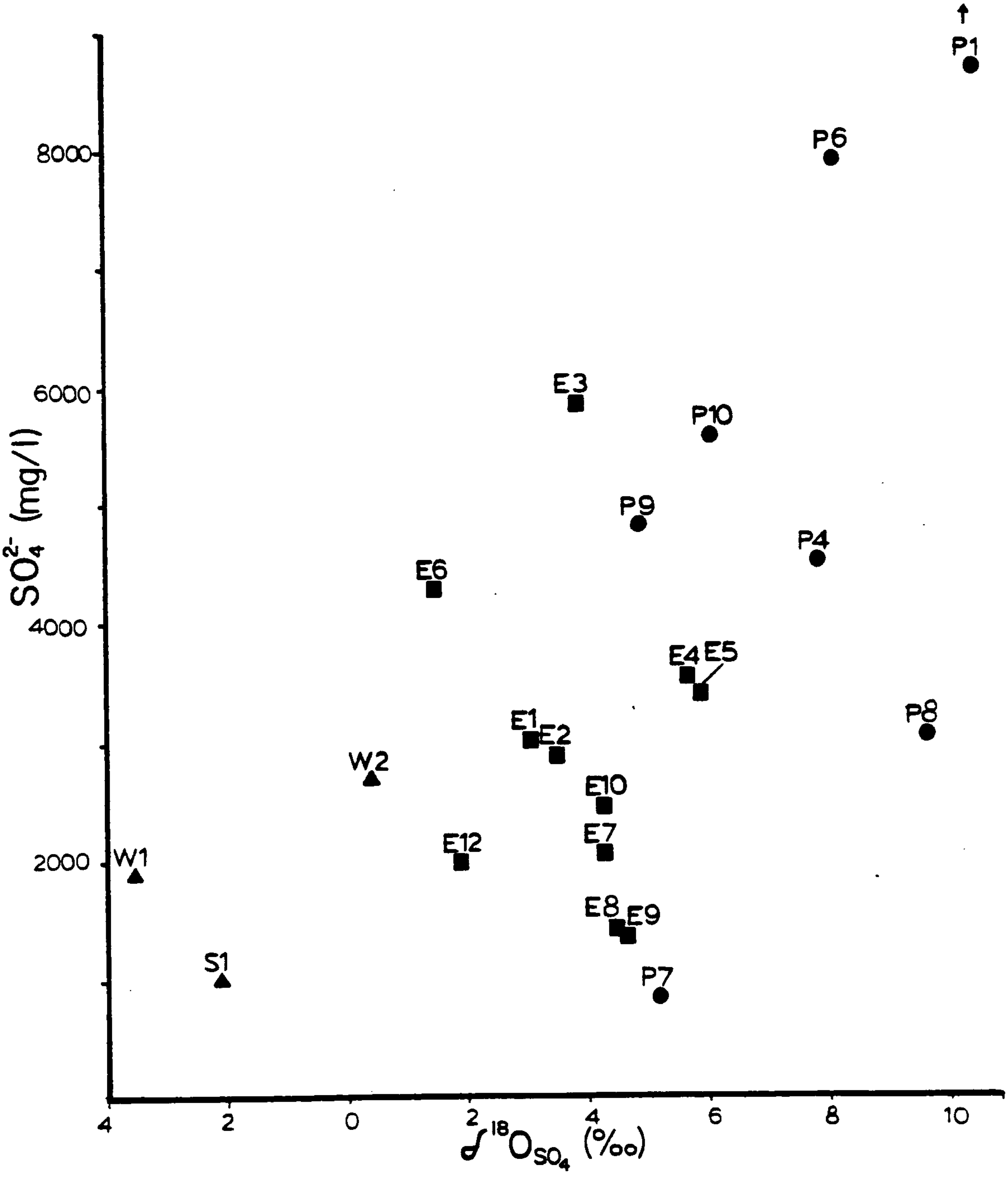


Figure 15. Sulfate versus $\delta^{18}O$

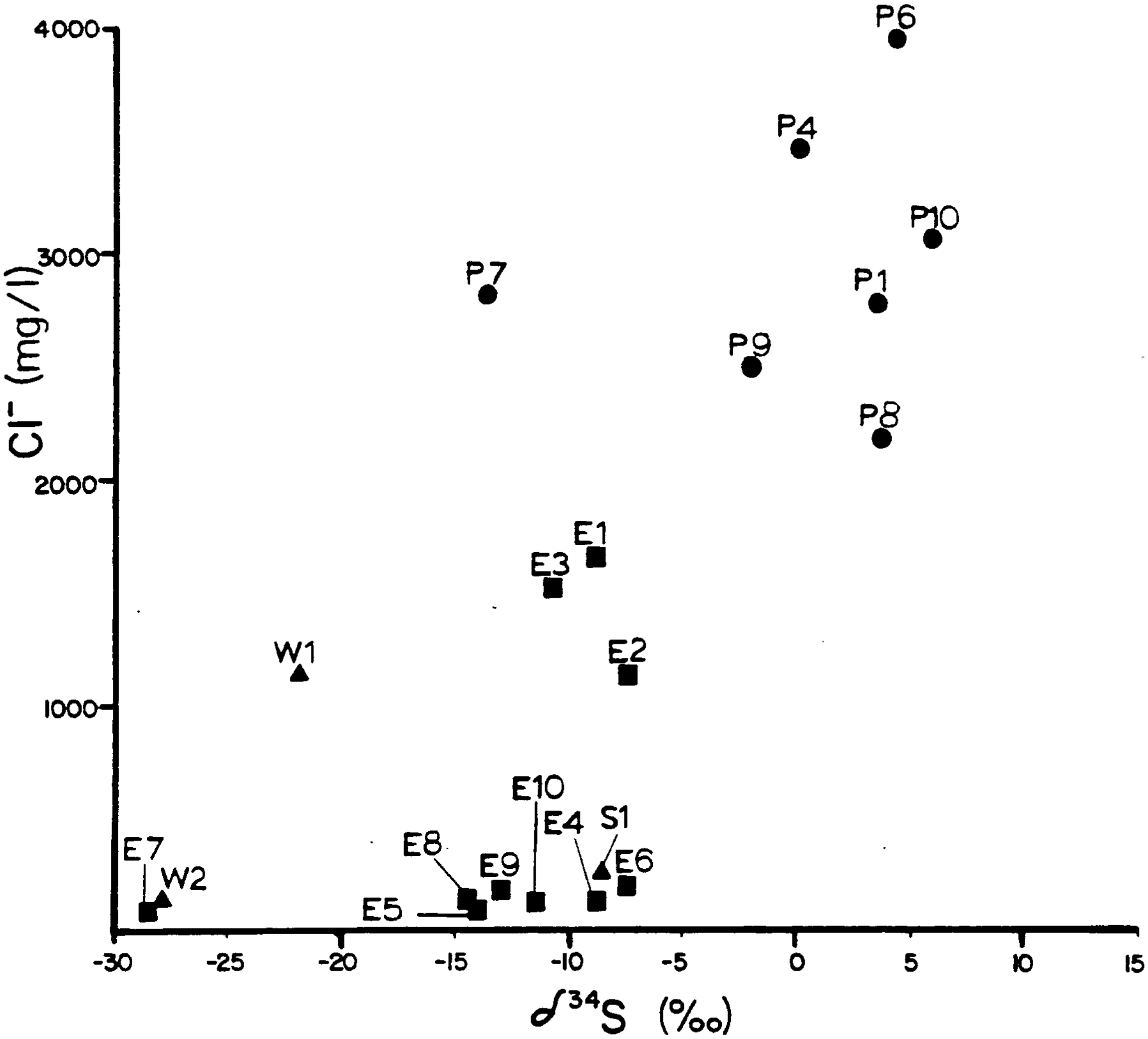


Figure 16. Chloride versus $\delta^{34}S$

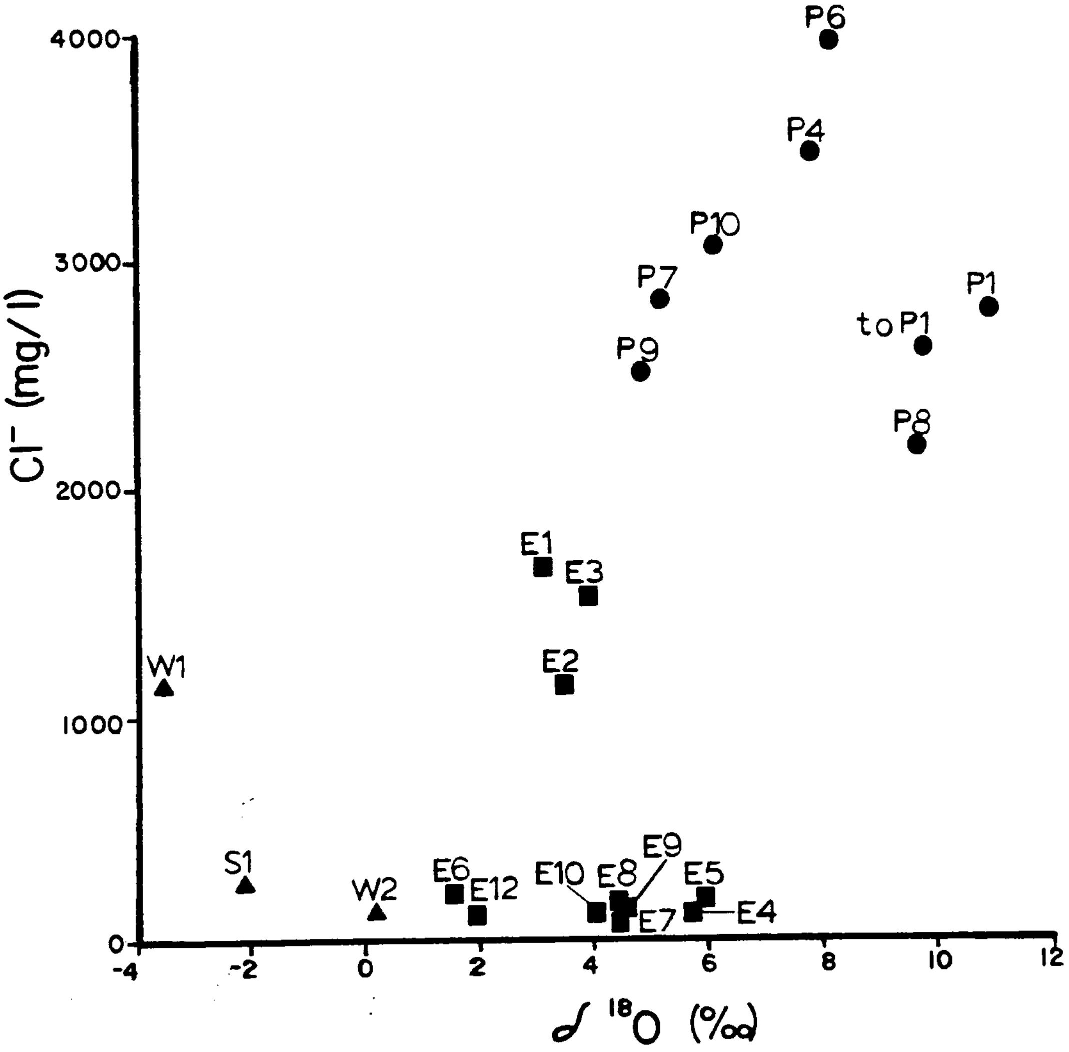


Figure 17. Chloride versus $\delta^{18}O$

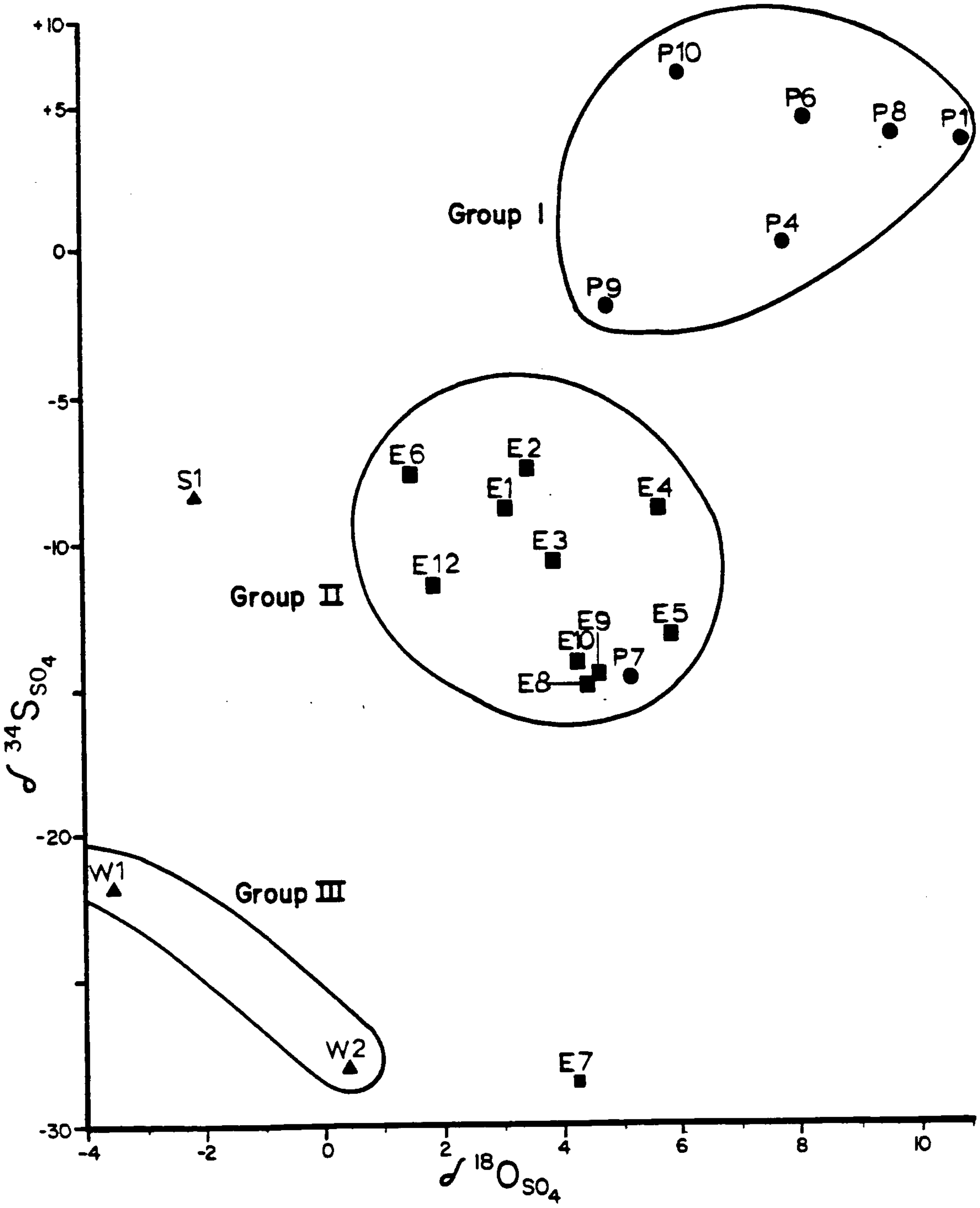


Figure 18. Sulfur-34 in dissolved sulfate versus $\delta^{18}O$

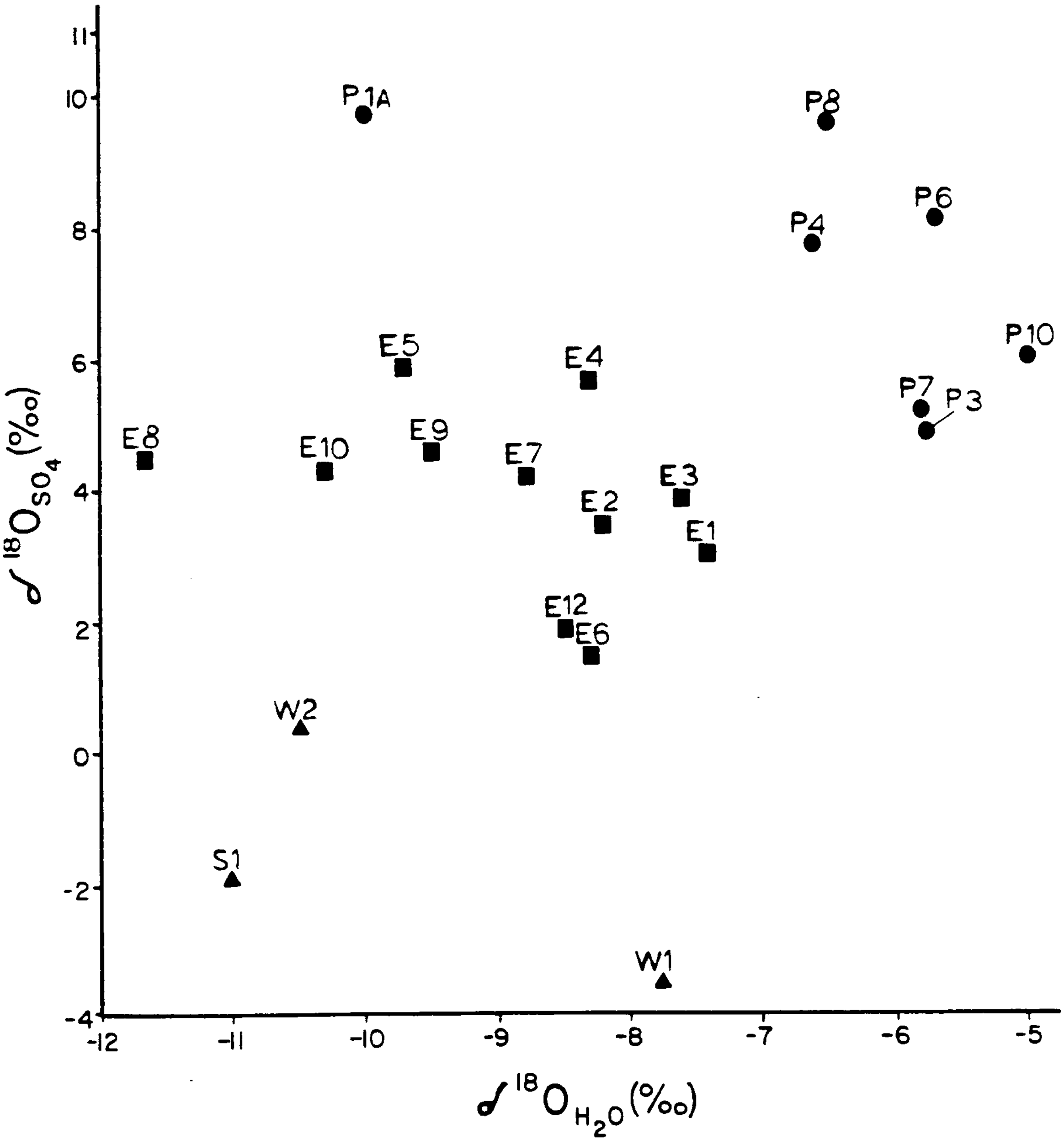


Figure 19. Sulfate $\delta^{18}O$ versus water $\delta^{18}O$

Mixing Theory

If a water sample contains concentration C_m of a conservative solute derived from n sources and each source has a characteristic solute concentration $c_1, c_2, \ldots, c_n$ and a characteristic isotopic composition $\delta_1, \delta_2, \ldots, \delta_n$, then by mass balance:

$$C_m = \sum_{i=1,n} c_i x_i \tag{1}$$

where x is the fraction of each source in the sample so that:

$$\sum_{i=1,n} x_i = 1 \tag{2}$$

Similarly, the isotopic composition of the sample is:

$$\delta_m = \sum_{i=1,n} (c_i \delta_i x_i)/C_m \tag{3}$$

If a solute has two isotopic values associated with it such as in sulfate, δ^S_m and δ^O_m, these values can be plotted against each other so that discrete groups of points will show solute sources, thus defining δ_i. A sample containing a mixture of two sources will plot along the mixing line between two sources. A sample containing a mixture of three sources will plot within the area defined by three mixing lines. If a sample then contains a solute from three or less sources, the fraction of each solute, x_i, can be uniquely determined by simutaneous solution of equations (1), (2), and (3).

Water Sources

Figures 14-17 show relationships between sulfate isotopic composition and sulfate and chloride concentration in millsite samples.

Sulfate and chloride are generally regarded as conservative tracers in that they travel with the ground-water plume. Sulfate concentrations of all millsite samples except one are greater than 1,000 mg/L, so that c_i for each source contributing sulfate to the alluvium is not unique. High chloride concentration, however, is associated with the mill pond leachate, so that pond leacheate waters can be distinguished from other waters. Chloride presentlly added in the milling process is 45,000 mg/L, and discharge to the tailings pond has a chloride concentration of 1,500 to 3,000 mg/L. Chloride content of mine waters averages only 50 mg/L.

Figure 18 shows the relationship between $\delta^{34}S$ and $\delta^{18}O$ of sulfate in millsite samples. The heterogeneous isotopic distribution characterizes three fairly distinct groups of dissolved water (Groups I, II, and III). The data along with a cursory knowledge of the mill discharges supports an interpretation of three sources of water recharging the alluvium containing sulfates of distinctive range in isotopic composition: (1) pond seepage, (2) mine dewatering discharge, and (3) flow from the Tres Hermanos Sandstone Member. Pond seepage and mine dewatering discharges are known uranium industry effluents recharging the alluvium. The third water source, purported to be the flow from the Tres Hermanos, was revealed only through sulfate isotopic analyses. These groups of water are found in localized areas around the millsite (fig. 13).

Considerable scatter of sulfate isotope values exists in the designated water groups. A much smaller spread in delta values would be expected in well-mixed water sources such as pond seepage or mine discharge formation waters. However, each water source listed above contains sulfates of different origin and thus different isotopic values. These sulfate components have varied spatially and temporally, so that waters of the same source may not be expected to have narrowly defined sulfate isotopic signatures. The following section looks at the possible sulfate components in each of the three water sources.

Sulfate Sources

Group I (fig. 18) can be termed "pond leachate." This group carries the heaviest isotopic values for both sulfur and oxygen. Pond leachate contains sulfate from three origins:

1. Chemical; acid sulfate (H_2SO_4).
2. Mineral; oxidized sulfides.
3. Ground water; dissolved sulfate.

The isotopic signature of Group I waters can be expected to vary with the relative proportions and isotopic value of each sulfate source.

The mill's sulfuric acid is manufactured at the Kerr-McGee millsite from elemental sulfur presently obtained from sour gas (H_2S) processing plants in Oklahoma. Isotopic values for the final product acid depend on the original $\delta^{34}S$ of the H_2S, the incorporation of oxygen into the sulfate, and the fractionating processes occurring along with production steps.

Pond sulfates of mineral origin are produced by oxidation of mineral sulfides, both in the mill circuit and in the pond waters. Metal sulfides, common in ore, become oxidized under low pH conditions to metal oxides plus sulfate:

$$M^*S + 2H^+ = M^{2+} + H_2S^o\ (aq) \quad (4)$$

$$2M^{2+} + 2H_2S + 7H_2O = M_2O_3 + SO_4^{2-} + 16H^+ + 10e^- \quad (5)$$

where M* = generic symbol of common metal forming sulfides.

Pyrite and marcasite (FeS_2) are the most common sulfide minerals associated with ore in the Grants region (Laverty and others, 1963). Pyrite in the mill circuit, and when released to the surface environment tailing pond in a finely divided form, becomes oxidized, releasing large amounts of iron and sulfate to the pond waters and lowering the pH. The reaction is:

$$2FeS_2 + 7O_2 + 2H_2O = 2Fe^{2+} + 4SO_4^{2-} + 4H^+ \quad (6)$$

The concentration of iron (Fe^{2+}) measured November 9, 1981 in Pond #1 and reported as 3,870 mg/L by the New Mexico State Laboratory, Albuquerque, shows the significance of reaction (6) in contributing some sulfate to the pond waters.

The $\delta^{34}S$ was measured on a sample of the sulfuric acid used in the mill circuit, because this was expected to be the primary source of sulfate in pond leachate. The value was +5.8°/oo. The $\delta^{34}S$ value for tailings pond water (Pond #1) was +3.7°/oo. This lowered value may be reconciled by the addition of lighter sulfate sulfur from oxidation of sulfide minerals (e.g., pyrite) or from dissolved sulfate in ground waters used in the mill processing. Sulfates of mineral origin and ground-water origin could have a wide range of values. Jensen (1958) and Warren (1972) have looked at mineral and dissolved sulfur isotopes in investigations of ore processes that concentrate ore trends of uranium like those found in the Grants region. If reaction (6) is significant, it is expected that the sulfate oxygen would bear some relationship to the water oxygen (Robinson, 1973; Schwarcz and Cortecci, 1974). Neither the pond water nor the sulfate oxygen-18 values were obtained; therefore, no reasonable relationships can be derived from the smattering of sample points in Group I (fig. 19).

Another factor, normally not considered in natural water systems but which must be addressed in considerations of Pond #1 waters, is isotopic fractionation by exchange reactions between water and sulfate oxygen (Lloyd 1967, 1968). This exchange reaction is markedly quickened by decreasing the pH (Hoering and Kennedy, 1957) and increasing the concentration of bisulfate. At the pH of 1.4 measured in Pond #1, the bisulfate ion (HSO_4^-) is the predominant sulfur species (Garrels and Naeser, 1958). It is through this ion rather than sulfate (SO_4^{2-}) that an oxygen exchange with water can readily take place. The oxygen exchange mechanism is believed to be acid-catalyzed dehydration (Radmer, 1972) that proceeds through the following reactions (Hoering and Kennedy, 1957):

$$H^+ + HSO_4^- = H_2SO_4 \qquad \text{rapid}$$

$$H_2SO_4 = H_2O + SO_3 \qquad \text{slow}$$

where exchange between water and bisulfate (HSO_4^-) can take place at a $t_{\frac{1}{2}}$ exchange rate in terms of hours.

Lloyd's (1968) experimental data for oxygen exchange in the sulfate–water system yielded the relationships:

$$\ln \alpha_{SO_4{}^{2-}{}_{soln} - H_2O} = (3251/t^2) - 0.0056$$

Substituting the temperature for Pond #1, 288°K, into the relationship, the expected equilibrium fractionation factor for dissolved sulfate–water is 34°/oo.

The sulfate $\delta^{18}O$ measured in Pond #1 was +11.0°/oo (table 5), so the expected $\delta^{18}O$ for water in equilibrium with sulfate is -23.0°/oo. The water $\delta^{18}O$ (table 5) measured for water discharged into Pond #1 was only -10°/oo, suggesting that the sulfate and water are not in equilibrium and that $t_{\frac{1}{2}}$ exchange rates may be considerably longer than hours. Acid sulfate added in the milling circuit has only been in contact with the water for a short period of time before water is discharged into Pond #1, so equilibrium may not be reached in mill discharge waters. A more reliable $\delta^{18}O$ value would be from water in Pond #1, which has had a longer time to equilibrate with acid sulfate added in the milling process.

Mill solution entering Pond #1 and solution in Pond #1 were analyzed for solution $\delta^{18}O$. Sulfate exiting directly from the mill had a solution $\delta^{18}O$ of 9.8°/oo, whereas pond sulfate had a $\delta^{18}O$ of 11.0 °/oo. This change may not be due only to oxidation of sulfide minerals in the tailings, but to rapid exchange between the water and sulfate oxygen under the low pH conditions. Incomplete data prevent any estimation of relative importance of exchange reactions. If exchange were significant, the water $\delta^{18}O$ and sulfate $\delta^{18}O$ would correlate just as possible for sulfide mineral oxidation. Figure 19 shows some slight trend within Group I waters. Mill discharge to Pond #1 sits farthest outside the designated Group I waters, suggesting either that most of the water–sulfate exchange takes place within the pond or that sulfide mineral oxidation plays a significant role only after waters are discharged into Pond #1. Because mill circuit pH is 0.5 (Kerr-McGee, 1982, personal commun.), it is expected that a considerable amount of oxygen exchange would take place within the milling cycle before discharge (Hoering and Kennedy, 1957). Calculated equilibrium fractionation factors do not support a large amount of exchange within the mill circuit. Sulfide mineral oxidation within the ponds and the incorporation of water molecule oxygen and dissolved oxygen into the product sulfate seems to be an important reaction.

Group III waters (fig. 18) can be designated as waters from the Tres Hermanos sandstones. Only the isotopes designate these waters as a distinct and common group. Water chemistries of all three samples (table 5) are very different and would not commonly characterize these waters. This group is sparsely defined, only three points were sampled with one falling outside the group boundaries. Both wells W1 and W2 are completed in the Tres Hermanos-B sandstone west of Arroyo del Puerto. The surface water sample S1 is taken from Arroyo del Puerto less than 1,000 ft south of wells W1 and W2. This sample lies outside Group III due to its high $\delta^{34}S$ value (fig. 18). Sample S1 is placed in Group III based on its position in figure 19 with the lightest water $\delta^{18}O$ and sulfate $\delta^{18}O$ of any sample. The low water $\delta^{18}O$ confirms that the river is carrying water of ground-water origin rather than meteoric or surface water. The water $\delta^{18}O$ values would be expected to be high in surface waters due to kinetic evaporation processes. The low sulfate concentration (1,034 mg/L) compared to almost all other samples, makes the river more susceptible to changes in sulfate isotopic composition due to inputs from varying sulfate sources. The position of S1 in figure 18 is largely subject to temporal variations in sulfate input due to short residence time of a dissolved constituent at a given point along a river.

Although point S1 is known to be receiving waters from mine discharge, much of the sulfate from this source is removed in the coprecipitation of radium before waters are discharged to Arroyo del Puerto (Ganus, 1980). If much of this sulfate is removed, then other sources such as the inflow from the Tres Hermanos Sandstone Member becomes important in defining an isotopic ratio. High sulfate concentrations (2,500 mg/L) are typical of Tres Hermanos water in the Ambrosia Lake area (Brod, 1980), and this sulfate source may be a significant component in the river waters at this point. This is certainly supported by the sulfate isotope results.

The Tres Hermanos-B layer crops out and caps the small hills west of Arroyo del Puerto (fig. 8). Most of the rock has become highly weathered and is mapped as saprolite. High sulfate content in these waters may be from dissolution of weathered Mancos host rock. These marine shales may have originally contained biogenic sulfides with very low $\delta^{34}S$ values. Biogenic sulfides within close proximity may be expected to have a wide range in $\delta^{34}S$ values (Warren, 1972). The oxygen incorporated into the sulfate may also be expected to vary.

Lloyd's (1968) experiments showed that oxidation of sulfide to sulfate in nature is a complex process, incorporating both water oxygen and molecular oxygen. The oxidation takes place in at least two steps, and predictions of oxygen isotopic effects are complicated by isotopic exchange of intermediate phases with the water.

The high chloride content (1,130 mg/L) and higher $\delta^{34}S$ of the water in sample W1 suggest possible influence of pond seepage in this well. The flow net (fig. 11) shows that these wells are not likely to intercept pond seepage, but several faults in this area west of the river may provide conduits for seepage migration (figs. 8 and 6).

Group II (fig. 18) waters compose the bulk of the samples analyzed for $\delta^{18}O$ and $\delta^{34}S$ in sulfate. According to mixing theory, their position between "light" Tres Hermanos waters and "heavy" pond leachate waters would designate this group as mixtures of Group I and Group III waters. This conclusion is invalidated by basic hydrologic flow principles and because the isotopic data do not lend themselves to the proposed mixing model.

According to mixing theory, the relative proportions of water sources can be determined in each mixed sample based on chemical and isotopic data. The problem in applying this model is that end-member groups are not clearly defined so that each water source does not have a unique concentration of a conservative tracer (c_i), or isotopic signature (δ_i). If c_i and δ_i cannot be uniquely defined for each source, i, then the fraction of each source (x_i) in a mixed sample will be multiplied by the uncertainty of c_i and δ_i.

If a conservative tracer such as sulfate carries two isotopic signatures in a mixed sample:

$$\delta_m^O = \sum_{i=1,n} (c_i \delta_i^O x_i)/C_m \tag{7}$$

$$\delta_m^S = \sum_{i=1,n} (c_i \delta_i^S x_i)/C_m \tag{8}$$

where δ_m^O is the oxygen-18 value and δ_m^S is the sulfur-34 value for the mixed sample. The equations can be related by concentration of sulfate in the sample C_m. The resulting relationship is:

$$\frac{\delta_m^O}{\delta_m^S} = \frac{\sum_{i=1,n} (c_i \delta_i^O x_i)}{\sum_{i=1,n} (c_i \delta_i^S x_i)} \tag{9}$$

Because c_i for each sulfate end member is the same, the relationship can be simplified to:

$$\frac{\delta_m^O}{\delta_m^S} = \sum_{i=1,n} \frac{(x_i \delta_i^O)}{(x_i \delta_i^S)}$$

and

$$\sum_{i=1,n} x_i = 1$$

So that the measured ratio of $\delta^{18}O$ to $\delta^{34}S$ for sulfate or its location on figure 18 can be used to determine x_i or the fraction of pond leachate and formation water in a water sample. In this manner, the uncertainty of x_i is reduced by eliminating the c_i factor.

The problem still inherent in applying this model is that both Group I and Group II waters contain mixtures of sulfate of different origins and isotopic composition so that end-member delta values (δ_I and δ_{III}) cannot be chosen for each water source. If arbitrary "average" end-member delta values are chosen for Groups I and III, only those mixed samples that fall on a line directly between these points can be solved for mixing proportions, x_I and x_{III}.

Hydrologic information does not support the position that all these samples are mixtures of Tres Hermanos and pond seepage waters, with a relatively greater proportion contributed by pond leachate. The estimated gradient to the east and south, respectively, is only 12 and 22 ft/yr (see figure 11). It is highly unlikely that pond seepage migrated as far as well E6. Arroyo del Puerto also acts as a hydrologic boundary to prevent mound build-up beneath the ponds (Ganus, 1980) so that gradients east of the river are reduced.

Group II waters, all located east of Arroyo del Puerto, except for P7 are designated as mine discharge waters. These waters all have highly variable chemistries (table 5). The sulfate isotopes are very important in establishing this group of waters.

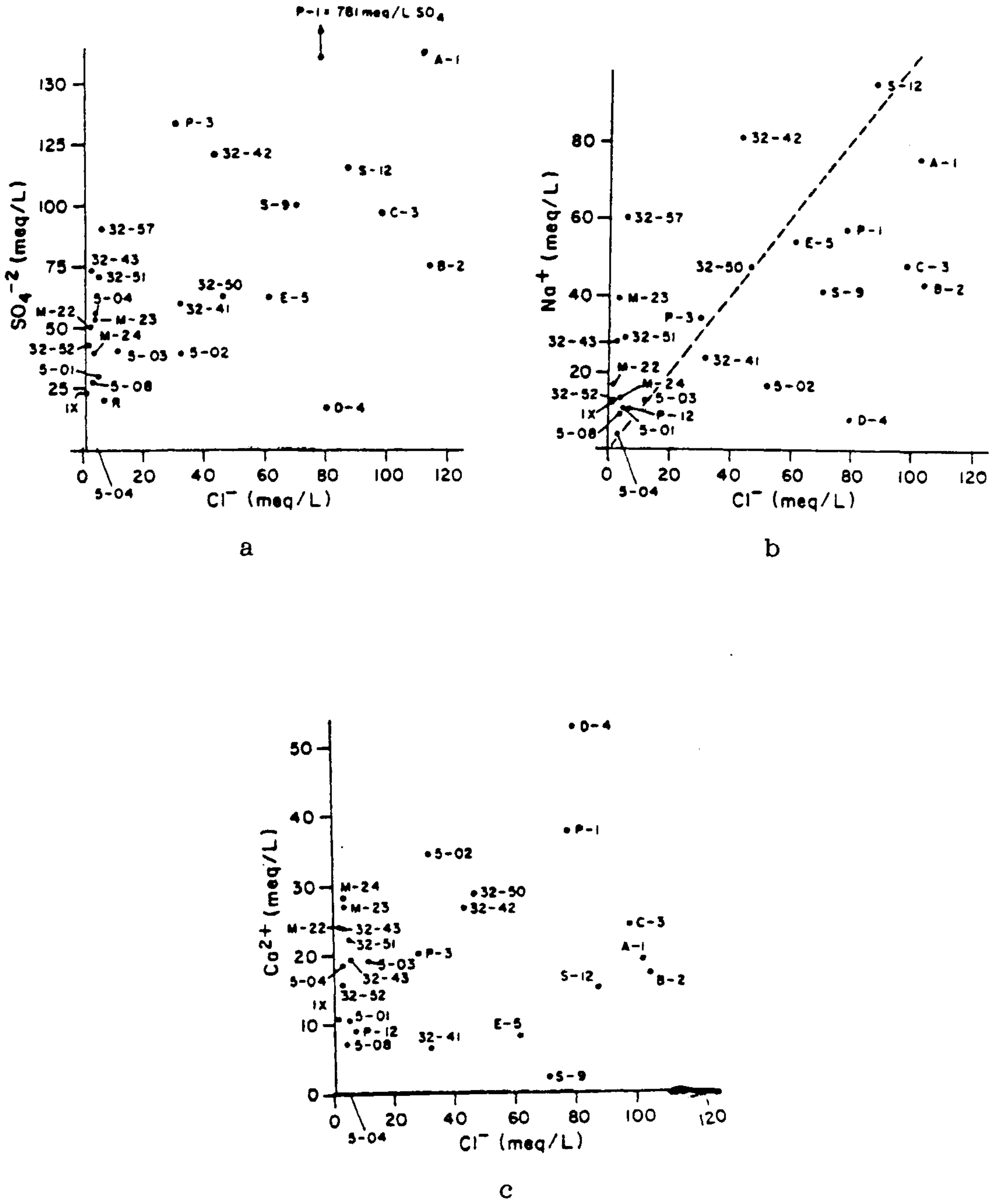
Mine discharge contains sulfates dissolved in formation waters of the Westwater Canyon Sandstone, the Dakota Sandstone, and the Tres Hermanos sandstone layers of the Mancos Shale. Each formation may logically contain sulfate of different origin and history, consequently, of different isotopic composition. Although formation waters become well mixed before discharge from the mines, the relative proportions of the different waters pumped from the mines varies with location and construction of the mine in relation to the hydraulic properties of the penetrated formations.

The sample representative of mine discharges at the date of collection is the mill reservoir (labeled S2) in table 5. Water pumped from mines is conveyed via unlined ditches to the mill reservoir for use in the mill process. Excess mine drainage is diverted into Arroyo del Puerto after suitable levels of radium are obtained. Unfortunately, sulfate $\delta^{18}O$ was not obtained for sample S2, so its value is conspicuously missing from the Group II waters. It is suspected from its chemistry that this point would lie near S1 on figure 18 and its sulfate $\delta^{18}O$ would be less affected by radium precipitation and consequent sulfate removal.

Sample P7 (D4) differs both chemically (table 5) and isotopically (fig. 18) from other pond monitor wells and is included in Group II waters. This well is believed to be completed in the Mancos Shale (Canus, 1981, personal commun.), which may contain saturated lenses or likely provide an effective chemical exchange barrier mechanism as pond leachate percolates through the shaly layers. Ion exchange reactions can be significant in clayey materials.

Sulfate concentration in P7 (D4) is 867 mg/L, the lowest value observed, whereas chloride concentration is 2,837 mg/L (figs 14-17). If chloride concentration is an accurate indication of pond seepage, the Mancos must have some highly effective mechanism for sulfate removal either by adsorption or precipitation.

Ion exchange effects are indicated by the water chemistry shown in figure 20. On fig. 20b, sodium, which in pond seepage



a

b

c

Figure 20. Comparison of water chemistry analyses in the vicinity of the Kerr-McGee Ambrosia Lake uranium mill

should have nearly equivalent concentration with chloride falls far below the sodium chloride equivalence line (dashed line on figure 20B), whereas calcium (fig 20C) shows the highest concentration of all samples. This strongly suggests that sodium cations in pond seepage waters have replaced calcium cations in clay minerals, depressing sodium and raising calcium concentration above those in pond waters.

The low pH of 5.5 and low sulfate concentration in P7 (D4) suggest the occurrence of both reversible and irreversible exchange mechanisms. If sulfate in infiltrating waters is being removed by anion exchange, sulfate concentrations in P7 (D4) may be expected to increase in the future as exchange sites on the clay become filled. Future sulfate isotopic analyses could then be used to confirm the presence of pond seepage waters as sulfate isotope values increase.

The other anomalous sample is E7 (fig. 18), which may be considered to lie outside of Group II due to a lowered $\delta^{34}S$. This well is completed in the Tres Hermanos-B and may contain formation waters with lighter dissolved sulfate. This sample is included in Group II because of similar water $\delta^{18}O$ and sulfate $\delta^{18}O$ composition to other Group II waters (fig. 19). The light $\delta^{34}O$ may be accounted for by some local oxidation of sulfides near this site, producing sulfates with similar sulfate $\delta^{18}O$ values as the $\delta^{18}O$ of the water.

Notable in figures 16 and 17 is the high chloride concentrations that set wells E1, E2, and E3 apart from other Group II waters, indicating a possible mixing with Group I pond waters. The flow net (fig. 11) shows these wells are on the most northerly ground-water flow path from the ponds. From the flow net, assuming an average hydraulic conductivity for alluvium is 1.3 ft^2/day (Ganus, 1980) and an effective porosity of 20 percent, ground water may travel 35 ft/yr to the north compared to only 12 ft/yr to the east and 22 ft/yr to the southeast, delivering the pond leachate more quickly to more northern wells. Although no mixing proportions can be derived, these three sample points do lie nearer the Group I sample waters than other Group II waters.

CHAPTER 6

CONCLUSIONS

Each of the designated groups of waters, pond leachate, mine discharge, and Tres Hermanos water contains sulfate from different origins with different isotopic compositions. The concentrations of each sulfate component within a water group are subject to both geochemical and man-made controls. Therefore, the resulting sulfate $\delta^{18}O$ and $\delta^{34}S$ from mixtures of different origin sulfates may be expected to vary with time and location. Sulfate in pond leachate is removed by neutralization and adsorption reactions within natural substrata; sulfate in mine discharge formation waters is precipitated as $BaSO_4$ in the removal of radium in order to meet National Pollution Discharge Elimination System requirements (Ganus, 1980).

Unique sulfate $\delta^{18}O$ and $\delta^{34}S$ values cannot be assigned to waters of a designated group, therefore mixing theory cannot be applied to determine relative proportions of water groups within a mixed sample.

Although a quantitative calculation of mixing proportions cannot be made, a qualitative assessment of water types recharging the alluvium and their spatial relationships around the millsite can be made based on sulfate isotopes. This distinct grouping of waters would not have been possible based only on chemical data (table 5). Isotopes indicate that three types of waters are residing in the alluvium. These waters are designated as: Group I (pond leachate), Group II (mine discharge), and Group III (Tres Harmanos formation waters). Their relative locations in alluvium and surface-water samples from around the millsite are displayed in figure 13.

Based on sulfate isotopes, pond leachate waters have migrated only as far as P9. However, chloride concentrations (an even more conservative tracer) suggest that pond seepage has reached well W1 to the south (Group III) and wells E1, E2, and E3 (Group II) to the northeast.

Sulfate isotopes also implicated the importance of sulfide oxidation in pond waters. Monitoring of pond sulfate isotopes may help understand some of the geochemical reactions taking place within the ponds. Other geochemical reactions such as adsorption and ion exchange, occurring as seepage infiltrates the substrata may be monitored using sulfate isotopic values. For example, the adsorptive capacity of the Mancos Shale may be studied by watching for changes in sulfate isotopic ratios. Acidic tailings pond waters provide an interesting opportunity for further study on oxygen exchange rates in the sulfate–water system.

This study demonstrated the value of sulfate isotopic tracers in identifying different types of waters recharging an alluvial system. Extended isotopic monitoring may provide clues to the extent and the types of geochemical interactions occurring as seepage travels from impoundments into an aquifer system.

APPENDIX

PROCEDURES FOR SAMPLE PREPARATION, CONVERSION AND ANALYSIS

Procedures followed for sulfate isotopic analysis may be divided into steps for preparation of barium sulfate and steps for the thermal decomposition of barium sulfate to the required gas for isotopic measurement. A considerable portion of time was spent adopting and discarding laboratory techniques to obtain quantitative and reproducible isotopic results. This section is included to thoroughly outline perfected methodologies for sulfate isotopic analysis. Sulfur isotope analyses were performed at the University of Arizona Laboratory of Isotope Geochemistry. The preparation of carbon dioxide from barium sulfate for oxygen-18 analyses was performed at the U.S. Geological Survey Isotope Branch, Denver, Colorado, in the laboratory of Robert O. Rye.

Barium Sulfate Preparation

Equipment and Reagents

The materials used for the separation of sulfate from water samples included BioRad (Richmond, CA) prepacked 1.0 × 8.0-cm tapered columns filled with AG1-X8, 50-mesh, chloride-form strong base anion exchange resin and 50-ml disposable syringe barrels with tips to fit the exchange columns. Reagents required are 0.50 M NaCl, 0.25 M

$BaCl_2$, and 1:10 HCl solution. Millipore© (Bedford, Massachusetts) filtering apparatus was used to isolate the purified $BaSO_4$ precipitate.

Procedure

Sample measurement. Each filtered sample was measured for sulfate concentration, using a Hach Kit© (Loveland, Colorado) to determine sample volume to pass through each column without exceeding the exchange capacity. Column exchange capacity was approximately 123 mg SO_4^{2-}, and most of the samples required a 1:100 dilution to avoid sulfate breakthrough and a consequent small degree (1 - 2‰) of fractionation.

Ion Exchange and Elution. The sample is passed through ion-exchange columns to remove impurities that may coprecipitate with barium sulfate and produce traces of interfering gases during thermal decomposition. Syringes fitted to the columns were filled with diluted samples, which dripped (<2 ml/min) through the column. The unnaturally high chemical concentrations of these samples, even diluted, produced some yellow-to-brown precipitate bands near the tops of some of the columns and greatly reduced the dripping rate. Higher dilutions may have been warranted in the designated P samples. Eluent was checked for sulfate breakthrough using 5 ml of $BaCl_2$ solution. A cloudy precipitate ($BaSO_4$) indicated sulfate breakthrough, and a new column with a more dilute sample was used.

The sulfate was eluted from columns into 250-ml beakers with 100 ml of 0.5 M NaCl solution. To additionally guard against carbonate coprecipitation, the eluent was acidified to a pH of 2 with 1:10 HCl and then bubbled with compressed nitrogen to release carbonate as carbon dioxide.

Precipitation and Filtering. Twenty-five ml of $BaCl_2$ were stirred into each sample beaker to precipitate the purified sulfate as $BaSO_4$. The beakers were covered and precipitate allowed to settle overnight. The barium sulfate sample was filtered through a 0.45-μ cellulose acetate filter disc, using a Millipore© apparatus. The filter discs were dried in covered petri dishes at 105°C. Samples were transferred to small labeled vials. The $BaSO_4$ recovery was substantial in almost all samples so that painstaking transfer procedures were not necessary.

Sample Combustion

Barium Sulfate to Sulfur Dioxide Conversion

Mass spectrometric measurement of sulfate $^{34}S/^{32}S$ was made by converting $BaSO_4$ to sulfur dioxide (SO_2) by heating under vacuum to about 1,400°C in a quartz reaction tube. The overall reaction may be represented by the equation given by Holt and Engelkemeir (1970):

$$BaSO_4 \rightarrow BaO + SO_2 + \tfrac{1}{2}O_2.$$

Bailey and Smith (1972) also considered the following possible reactions:

$$BaSO_4 \rightarrow BaO + SO_3$$

$$SO_3 \rightarrow SO_2 + \tfrac{1}{2}O_2$$

However, mass scans on the final product gas indicated negligible mass-80 peak, hence negligible SO_3. The general methodology followed for the SO_2 preparation is presented by Bailey and Smith (1972) with modifications, namely the omission of the copper furnace.

Apparatus. Materials needed include a vacuum conversion line, a double-tipped oxygen-methane torch, and a prepared sample reaction tube (fig. A-1).

Procedure. The modified vacuum conversion line is diagrammed in figure A-1. The sample reaction tube is constructed of two pure quartz glass tubes: a 3-cm, 7-mm OD tube, which slips inside a larger, 12-cm, 9-mm OD tube. Twenty mg of the $BaSO_4$ sample were weighed into the inner silica tube, a tuft of pure quartz wool was gently tamped over the sample, and the tube inserted inside the larger tube. The reaction tube was then joined to the vacuum assembly by a 3/8-inch Cajon Ultratorr© (Cajon Company, Solon, Ohio) fitting. A sample vial was joined to the system, and the entire system was evacuated to 3 to 4 mtorr, indicated by two Pirani© (Bendix Corporation, Rochester, New York) gages. With Tap D closed, the reaction tube is gently heated with a gas flame emanating from the double-tipped torch positioned beneath the end of the reaction tube. The entire system remains open to high vacuum while the released water vapor (note gages) is pumped away. When the pressure registered by the gages began to level, then drop (about 10 min) a dewar of liquid nitrogen-ethanol (-83°C) is placed around the water trap to freeze any water vapor. The gages should once again display 3 to 4 mtorr.

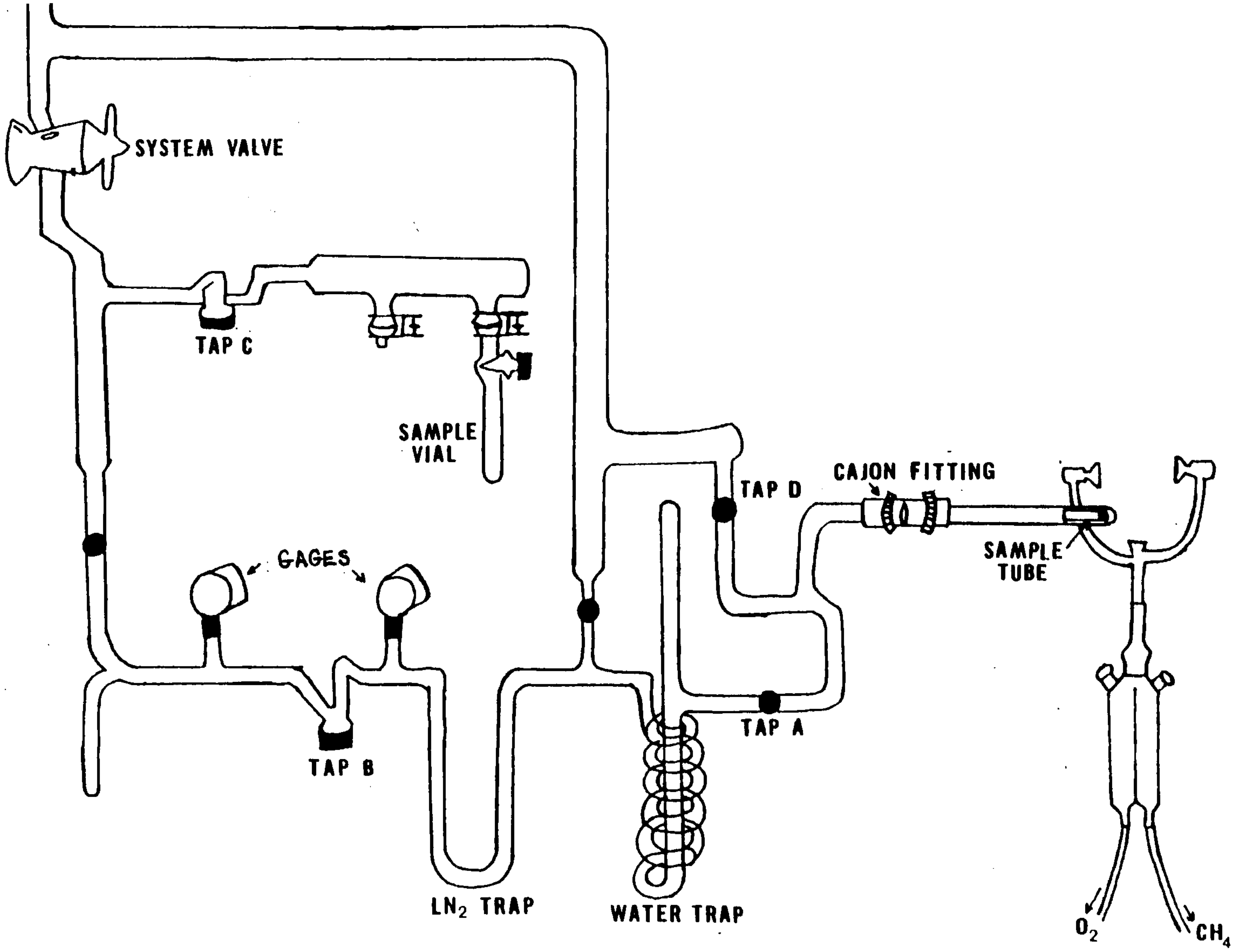

SYSTEM VALVE
TAP C
SAMPLE VIAL
GAGES
TAP B
LN$_2$ TRAP
WATER TRAP
TAP D
TAP A
CAJON FITTING
SAMPLE TUBE
O$_2$
CH$_4$

Figure A-1. Sulfur dioxide vacuum line

The sample was then ready for thermal decomposition. A dewar of liquid nitrogen was placed around the U trap. The torch flame was adjusted to an intense, sharply tipped flame (near melting point of quartz) to heat the reaction tube from the tip forward. The pressure rises, plateaus, then drops as the reaction nears completion. When the pressure returned to near 10 mtorr, the torch was removed, and Tap A closed. After the system once again reached 3 to 4 mtorr, the system valve was closed. The liquid nitrogen trap was removed and transferred to the sample vial, and the SO_2 gas condensed into the sample vial. When pressure read 3 to 4 mtorr, Tap C and then the sample valve were closed, and the vial removed from the assembly for mass spectrometric measurement.

The reaction tube was removed and replaced with a new sample tube; another sample vial was joined to the collection arm, and Taps C and A were opened to evacuate the system for another reaction. The water trap was removed after every other run and the coil heated to evaporate any collected water in the coils, which is then pumped out of the system.

The reaction must be quantitative to ensure no isotopic fractionation. Yields were measured on two initial samples, using a calibrated mercury manometer. Yields for both samples were greater than 95 percent.

Barium Sulfate to Carbon Dioxide Conversion

Mass spectrometric analysis for $^{18}O/^{16}O$ of dissolved sulfate is made by reducing $BaSO_4$ to BaS and producing carbon dioxide (CO_2).

The reaction of interest is:

$$BaSO_4 + 2C \rightarrow 2CO_2\ (+CO) + BaS$$

whereby more carbon monoxide (CO) is produced at higher temperatures and must be quantitatively converted to CO_2 by the following reaction:

$$2CO \rightleftarrows CO_2 + C$$

The methodology for the preparation of CO_2 is described by Nehring, Bowen, and Truesdell (1977).

Apparatus. The materials required include an internally heated resistance unit enclosed in a water-cooled Pyrex envelope, a heating current supplied by a high-current, low-voltage transformer connected to a variac. The resistance element is a small platinum foil boat (1 × 4 cm before folding) containing the $BaSO_4$ sample, and spectrographic-grade carbon. The CO conversion cell is connected to a neon-light transformer and a autotransformer for voltages up to 7,500 V. Figure A-2 shows the vacuum conversion line at the U.S. Geological Survey laboratory, Denver, and inset shows the reaction vessel resistance element.

Procedure. The platinum foil boat, stored in concentrated HCl, is rinsed thoroughly, then flamed over a Meeker burner, cooled, and tared. Twelve to twenty milligrams of barium sulfate are weighed and intimately mixed with an equal weight of spectrographic-grade carbon (-100 mesh) in a small agate mortar. The $BaSO_4$–C mixture is then carefully transferred to the boat and reweighed. The boat is pinched

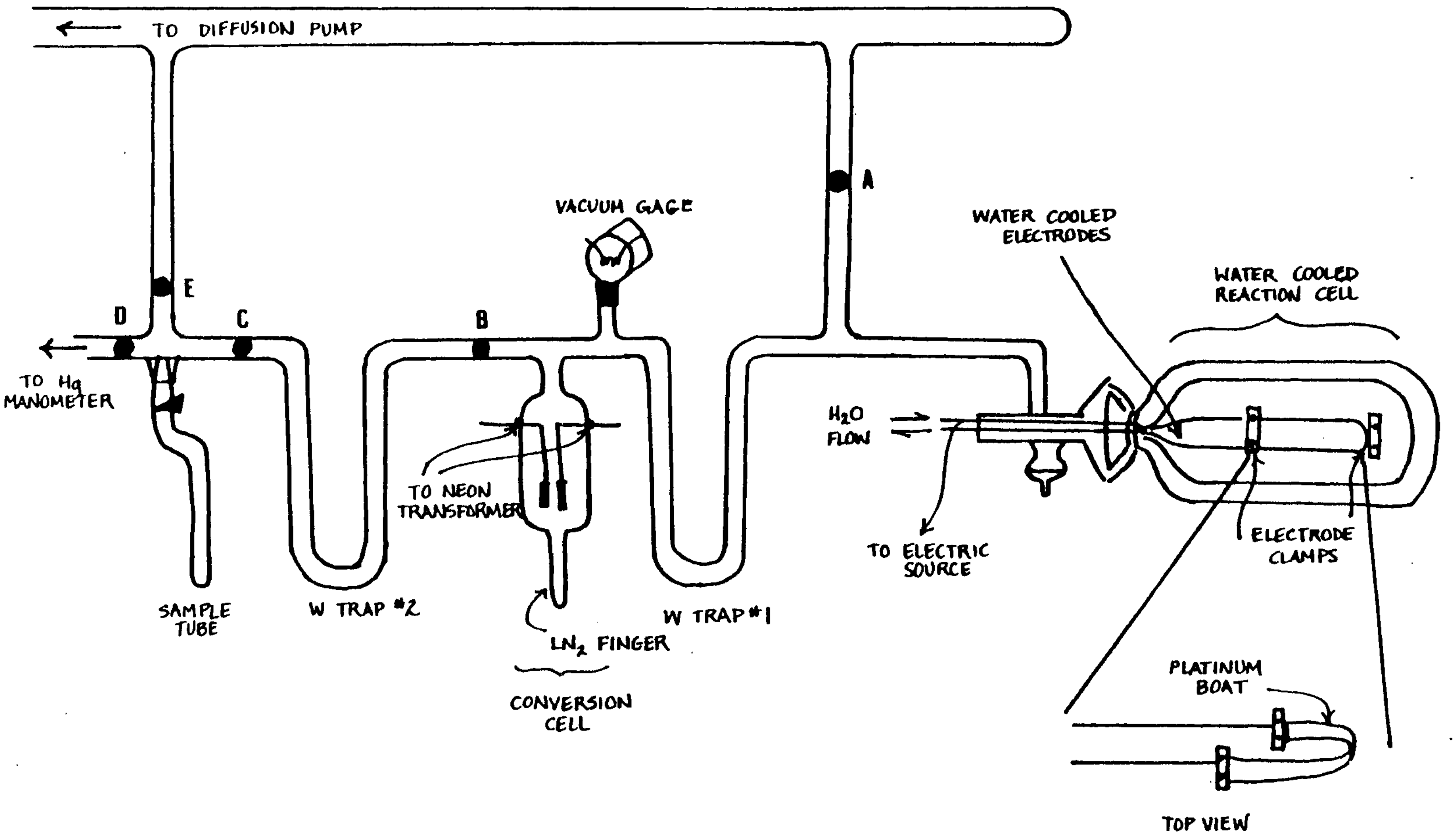

TO DIFFUSION PUMP
A
VACUUM GAGE
WATER COOLED ELECTRODES
WATER COOLED REACTION CELL
E
D
C
B
TO Hg MANOMETER
H_2O FLOW
TO NEON TRANSFORMER
TO ELECTRIC SOURCE
ELECTRODE CLAMPS
SAMPLE TUBE
W TRAP #2
W TRAP #1
LN_2 FINGER
CONVERSION CELL
PLATINUM BOAT
TOP VIEW

Figure A-2. Carbon dioxide vacuum line

shut and inserted into the electrode clamps of the resistance unit (fig. A-2).

The system is evacuated, then closed to the diffusion pump to check for leaks. The vacuum secure, Tap A is opened, Tap B closed, and Taps D and E opened. The sample is outgased at about 5 A for 10 to 30 min. Tap A is shut, so that the reaction portion of the line is isolated and liquid nitrogen (LN_2) is placed on W trap #1. The sample is heated by advancing the transformer by 2-A increments at 2-min durations up to 30 A for a maximum temperature of 1,050°C. The boat is held at 30 A for 4 min, and the voltage is turned off. A second LN_2 trap is placed on the conversion cell finger, and the voltage turned up to 5,000 V. A blue incandescence is observed around the electrodes. The blue color diffuses to the sides of the cell, then disappears as the pressure drops. The voltage is advanced to 7,500 V, and a blue flickering is observed. After this flickering subsides, the voltage is turned off, and the time of the conversion recorded (between 7 and 20 min).

Some CO may have been trapped with the CO_2 in W trap #1, so the CO_2 is liberated by removing both LN_2 traps, but replacing W trap #1 with a dry ice–ethanol trap to prevent the escape of water vapor. All CO_2 is then refrozen by replacing the LN_2 on W trap #1.

The $BaSO_4$ is seldom entirely converted during the first heating, so the transformer is switched on again to 30 A until the pressure rise ceases and no more rings form in the LN_2 trap. The voltage is then switched on again with LN_2 on the conversion cell finger and the pressure again drops as the blue flickering disappears. The dewars are topped with LN_2 and the final pressure recorded before Tap B is opened to pump away the noncondensibles with a dry ice–ethanol trap on W trap #2.

Tap E is closed, isolating the entire line from the vacuum, and Tap B (with D) is opened to vacuum distill the sample gas to the manometer finger for yield measurement. The sample gas is then transferred to the sample tube and is ready for mass spectrometric analysis.

Yields for the reaction were measured. using a mercury manometer and the following formula:

$$x = \left(\frac{\text{cm Hg rise} - 0.7237)}{0.0580\ (\text{wt BaSO}_4) \times 85\ \frac{\mu\text{moles CO}_2}{\text{mg BaSO}_4}} \right) \times 10^3$$

where x is the percent yield and wt $BaSO_4$ is weight transferred to boat. "Good" yields in the U.S. Geological Survey laboratory ranged from 100 to 120 percent. Samples with lower yields were suspect, and the conversion was repeated.

Analysis

Reporting Sulfur and Oxygen Isotopic Composition

Mass spectrometric measurements of sulfur isotopic composition are reported as delta sulfur-34 ($\delta^{34}S$), indicating the per mil deviation of the heavier isotope (sulfur-34) from the troilite sulfur in the Canyon Diablo meteorite (CD).

$$\delta^{34}S\ (^{\circ}/_{\circ\circ}) = \left(\frac{(^{34}S/^{32}S)_{\text{sample}} - (^{34}S/^{32}S)_{\text{CD}}}{(^{34}S/^{32}S)_{\text{CD}}}\right) \times 10^{3}$$

The Canyon Diablo international reference (CD) has a ^{34}S-^{32}S absolute ratio of 0.0450045 and its defined $\delta^{34}S$ value is $0^{\circ}/_{\circ\circ}$ (Nakai and Jensen, 1964).

Oxygen-18 measurements are reported as $\delta^{18}O$, indicating the per mil deviation of ^{18}O from the oxygen in a Vienna Standard Mean Ocean Water sample (V-SMOW):

$$\delta^{34}O\ (^{\circ}/_{\circ\circ}) = \left(\frac{(^{34}O/^{32}O)_{\text{sample}} - (^{34}O/^{32}O)_{\text{V-SMOW}}}{(^{34}O/^{32}O)_{\text{V-SMOW}}}\right) \times 10^{3}$$

In routine laboratory analyses, intermediate, or "working," standards are used whose isotopic compositions are known relative to the internationally defined standard, CD or V-SMOW. The working standards used in this laboratory were tank SO_2 gas for sulfur-34 measurements and CO_2 gas from a ^{14}C-dated bristle-cone tree ring sample for oxygen-18 measurements.

Machine Measurements

The mass spectrometer used in the University of Arizona Laboratory of Isotope Geochemistry is a dual collector Micromass, model 602-C, which allows the simultaneous collection of a major and a minor beam by two Faraday cups. The machine alternately measures the reference standard and the unknown sample to obtain an averaged "isotopic trace" for calculating the δ values.

The carrier gas for the isotopic measurements is SO_2 for ^{34}S and CO_2 for ^{18}O; therefore, the actual mass ratio measurements made in the machine are: mass 66/mass 64 for SO_2 and mass 50/mass 48 for SO, and mass 46/mass 44 and mass 45/mass 44 for CO_2. Because each of these gases carries an additional element with a variable isotopic mass, a correction must be made for ^{18}O in the case of ^{34}S analysis of SO_2 gas and for ^{13}C in the case of ^{18}O analysis for CO_2 gas.

The machine records the isotopic differences between the alternating reference gas and sample gas in the form of a set of traces on a strip recorder. The machine averages the differences between successive sets of traces. The $\delta^{66}S$ and $\delta^{50}S$ or $\delta^{46}O$ and $\delta^{45}O$ are calculated using these differences, the ratio control, and the offset.

Computations

Sulfur-34. The machine measurements for mass ratios of the carrier gas must be converted into δ values for the isotopes of interest, either $\delta^{34}S$ or $\delta^{18}O$. The equation for calculating $\delta^{34}S$ is:

$$\delta^{34}S = \left(\frac{2(50/48)_x - (66/64)_x}{2(50/48)_{ref} - (66/64)_{ref}} - 1\right) \times 10^3 \qquad (1)$$

where: 50/48 = mass ratio

x = sample

ref = working laboratory standard

The contribution of ^{18}O is corrected for by taking the difference between ratios measured on the $(50/48)_x$ for SO and the

66/64 peak for the SO_2. The SO peak (50/48) is multiplied by 2 so that all ^{18}O mass contributions cancel.

The mass 34/32 ratio for the standard Canyon Diablo is set at 0.0450 and the 34/32 mass of the working laboratory standard (tank (SO_2) was determined to be -1.8°/₀₀ with respect to Canyon Diablo by measuring against a series of isotopically "known" $BaSO_4$ samples obtained from the U.S. Geological Survey laboratory in Denver:

$$(34/32)_{ref} = (0.9983)(0.04500)_{CD}) = 0.04492 \qquad (1)$$

The $^{18}O/^{16}O$ of the reference tank SO_2 is still unknown, so a typical 18/16 (1/500 or 0.002) is assumed for calculating both $(50/48)_{ref}$ and $(66/64)_{ref}$. The $(66/64)_{CD}$ becomes 0.04900 (0.04500 + .002 + .002) and the $(50/48)_{cd}$ becomes 0.04700 (0.04500 + .002). The following ratios can be calculated for the tank gas reference:

$$(66/64)_{ref} = 0.04492 + 2(0.00200) = 0.04892 \qquad (3)$$

$$(50/48)_{ref} = 0.04492 + 0.00200 = 0.04692 \qquad (4)$$

These values, along with the Canyon Diablo values, can be fitted into equation (1) to obtain a $\delta^{34}S$ = -1.8°/₀₀, which represents the difference between the tank gas reference and the Canyon Diablo Standard, if an ^{18}O-^{16}O ratio of 0.002 is assumed.

Because the machine does not measure the absolute ratio of a sample but the difference with respect to the tank gas reference, the working equation for measuring the $(34/32)_x$ to the (34/32)tank gas (ref) is:

$$\frac{^{34}R_x}{^{34}R_{ref}} = \frac{2(0.04692)(^{50}\delta_{x/ref}/10000 - 1) + 0.04892(^{66}\delta_{x/ref}/1000 + 1)}{0.04492} \qquad (5)$$

where: $^{34}R = (34/32)$.

and the machine measures the $^{50}\delta$ x/tg and the $^{66}\delta$ x/tg as described previously. For reporting values, the mass–34 ratio of the sample compared to the mass–34 ratio of the Canyon Diablo Standard can be easily evaluated by the following equation using the relationship shown by equation (2):

$$\frac{^{34}R_x}{^{34}R_{CD}} = \frac{^{34}R_x}{^{34}R_{ref}} \times \frac{^{34}R_{ref}}{^{34}R_{CD}} = \frac{^{34}R_x}{^{34}R_{ref}} \times 0.9983 \qquad (6)$$

The final $\delta^{34}S$ of the sample with respect to Canyon Diablo may be expressed as:

$$\delta^{34}S_{x/CD} = \left(\frac{^{34}R_x}{^{34}R_{CD}} - 1\right)10^3 \qquad (7)$$

Combining equations (5), (6), and (7), so the reported value $(S_{x/CD})$ can be computed by a single relationship, gives:

$$\delta^{34}{}_{x/CD} = (0.9983)(2(0.04692)\ \frac{^{50}\delta_{x/ref}}{1000} + 1)$$

$$- (0.04892(\frac{^{66}\delta_{x/ref}}{1000} + 1)) - 1)10^3 \qquad (8)$$

To avoid the repetitious handling of equation (8) and the ratio calculations, a computer program directly calculates the $\delta^{34}S_{x/CD}$ by inputting the decade settings, offset settings, and digital voltmeter readings. Sulfate oxygen-18 values were computed by equations with a similar format (Craig, 1967).

Sulfur-34

The relationship between the tank gas and the Canyon Diablo Standard shown in equation (2) was produced by running a series of barium sulfate standards (+3.2°/$_{oo}$) obtained from Robert O. Rye at the U.S. Geological Survey Isotope Branch laboratory in Denver. If the $^{34}S_{x/CD}$ is known, working backward from equation (7) the $^{34}R_x/{}^{34}R_{CD}$ can be expressed. Measuring the known standard and fitting the machine values into equation (5), a value is obtained for $^{34}R_x/{}^{34}R_{tg}$. If both $^{34}R_x/{}^{34}R_{tg}$ and $^{34}R_x/{}^{34}R_{CD}$ are known, the $^{34}R_{tg}/{}^{34}R_{CD}$ can be calculated from equation (6). Table A-1 shows the series of $\delta^{34}S$ values measured for the standard Baker $BaSO_4$ samples.

This laboratory produced a slightly higher value for the Baker standard with a precision of ± 0.3°/$_{oo}$. From the $\delta^{34}S_{x/tg}$ = +3.7°/$_{oo}$ and the $\delta^{34}S_{x/^{34}CD}$ = +3.2°/$_{oo}$, the value for $\delta^{34}S_{tg/CD}$ was found to be -2°/$_{oo}$, and the 0.9983 constant in equation (8) was adjusted to 0.9977 to obtain the +3.2°/$_{oo}$ value for $\delta^{34}S_{x/CD}$.

Oxygen-18

Two San Gregario sea-water standards were run to check for accuracy of the oxygen-18 ratios. The average value for nine samples run at the U.S. Geology Survey Isotope Branch laboratory in Denver was +8.7°/$_{oo}$. Prepared CO_2 samples run at the University of Arizona

Table A-1. Sulfur values for Baker reagent $BaSO_4$.-- +3.2$^{\circ}/_{oo}$ U.S. Geological Isotope Branch laboratory, Denver, Colorado

Trial	$\delta^{34}S$ ($^{\circ}/_{oo}$)
1	+3.04
2	+3.42
3	+3.93
4	+3.84
5	+3.70
6	+4.08
7	+3.99
Mean	+3.71 ± 0.34

Laboratory of Isotope Geochemistry gave reproducible values of 8.1$^{\circ}/_{oo}$ and 8.2$^{\circ}/_{oo}$.

Yields measured on all samples ranged from 113$^{\circ}/_{oo}$ to 129$^{\circ}/_{oo}$, which were considered "good" yields (100$^{\circ}/_{oo}$-123$^{\circ}/_{oo}$) on the U.S. Geological Survey oxygen line.

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